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Fate Of Coated Zinc Oxide In Municipal Solid Waste Landfills

Stephanie Carbone Bolyard
University of Central Florida

FATE OF COATED ZINC OXIDE NANOPARTICLES IN LANDFILL LEACHATE

by

STEPHANIE CARBONE BOLYARD
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ABSTRACT

Given the increase in nanomaterial (NM) use in consumer products and the large fraction of waste placed in landfills worldwide, the probability of these products reaching municipal solid waste (MSW) landfills at the end of their useful life is high. Since nanotechnology use is still in its early stages, there are currently no regulations pertaining to the disposal of NMs and their fate in MSW landfills is still unknown. Understanding the fate of NMs in MSW landfills is vital to ensure the proper handling of these novel materials from cradle to grave; such research will provide information on how these NMs can be safely introduced into the environment.

This research seeks to understand the fate of NMs within waste environments by examining the interactions between NMs and landfill leachate components. The primary focus of this thesis is the effect of Zinc Oxide (ZnO) on biological landfill processes, solids aggregation, and chemical speciation of Zn in landfill leachate following the addition of crystalline, nano-sized ZnO coated with triethoxycaprylylsilane. This research (1) observed the effects of coated ZnO on five-day biochemical oxygen demand (BOD_5) and biochemical methane potential (BMP), (2) examined effects of solids aggregation on the fate of ZnO, (3) quantified the concentration of Zinc (Zn) by size fractions, and (4) modeled the chemical speciation of Zn in landfill leachate using Visual MINTEQ.

No change in dissolved Zn was observed after coated ZnO was exposed to “middle-aged” leachate. Upon exposure to “mature” leachate there was an increase in dissolved Zn assumed to be a result of the dissociation of ZnO. Solids data supported the aggregation of particles in both middle aged and mature leachate. There was an increase in the Zn concentration in leachate fractions greater than 1500 nm presumably due to the dispersion of normally insoluble ZnO

nanoparticles (NPs) following the interaction with humic acids (HA). ZnO did not inhibit anaerobic or aerobic processes in either middle aged or mature leachate, presumably due to the relatively low concentration of dissolved ionic Zn. Despite the observation of increased dissociation upon exposure to mature leachate, the presence of dissolved organic matter (DOM) may have hindered the ability for dissolved ionic Zn to become bioavailable.

Fractionation, BOD_5 and BMP tests, and chemical speciation modeling provided insight on the mobility of ZnO in landfills and the absence of inhibitory effects on landfill processes. Aggregation of ZnO NPs may prevent movement through traditional containment systems (i.e. geomembrane liners) due to the increased particle size. However, the increased dispersion suggests that ZnO NPs will be transported out of the landfill in the leachate, however biological treatment of leachate should be unaffected by the presence of ZnO. The bioavailability of Zn was not substantially affected by the presence of ZnO due to affinity of dissolved Zn for DOM. However, due to the heterogeneity of landfill leachate and the utilization of different NM coatings, it is challenging to predict the overall mobility of other NMs in a landfill.

I dedicate this thesis to my parents, Michael and Christina Carbone, grandparents, Robert and Violet Carbone and Jackie Massey, and last by not least my best friend and husband, Steven Bolyard in recognition of their moral support, immense patience, and everlasting pride in my accomplishment over the years.

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LIST OF ACRONYMS AND ABBREVIATIONS

BMP	Biochemical Methane Potential
BOD_5	Biochemical Oxygen Demand
CH_4	Methane
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
DLS	Dynamic Light Scattering
DOM	Dissolved Organic Matter
EDL	Electrical Double Layer
HA	Humic Acid
HDPE	High-Density Polyethylene
HRTEM	High-Resolution Transmission Electron Microscopy
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
LCA	Life-Cycle Assessment
MBRs	Membrane Bioreactors
MSDS	Material Data Safety Sheet
MSW	Municipal Solid Waste
NM	Nanomaterial
NOM	Natural Organic Matter
NP	Nanoparticle
SAED	Selected Area Electron Diffraction
SBRs	Sequential Batch Reactors
TCLP	Toxicity Characteristic Leaching Procedure
TSS	Total Suspended Solids
Zn	Zinc
ZnO	Zinc Oxide

INTRODUCTION

Over the last decade engineered particles with nanoscale dimensions have been key to advancements in drug delivery and pharmaceuticals, cosmetics, environmental remediation, nanotechnology, biomaterials, and energy production (Bhatt and Tripathi, 2011; Musee, 2011; Colvin 2003; Turco et al. 2008; Bittnar, Bartos et al. 2009; Sattler, 2011; Dreher 2004). Nanoparticles (NPs) are classified as having all three dimensions less than 100 nm (British Standards 2007; Linkov and Steevens, 2009; Sattler, 2011), whereas nanomaterials (NMs) have at least one dimension between 1 nm and 100 nm (Roco, 2003). NMs are commonly used due to their large surface area (Vollath, 2008) and unique electronic, optoelectronic, thermal, and catalytic properties (Linkov and Steevens, 2009). These unique properties are possible to the alteration of both chemical and physical properties as size is reduced (Farré et al., 2009). Most of the NPs that are incorporated into consumer products are coated, surface modified, and/or functionalized to achieve specific properties (Reinhart et al., 2010). According to an inventory completed by the Project on Emerging Nanotechnologies (Nanotech-Project, 2011) showed that 1,317 consumer products containing NMs were available in 2010. Of these products, just over 55% were health and fitness related and also included electronic components, cosmetics, antibacterial agents, polishing and binding agents, solar cells and UV-absorbers in sunscreen lotion, among many others (Linkov and Steevens, 2009).

It is estimated that the manufacturing of NMs will increase from 1,000 to 58,000 tonnes yearly from 2011 to 2020 (Royal Society and Royal Academy of Engineering, 2004). As NMs continue to be incorporated into consumer products the introduction of these materials into landfills and the environment is inevitable. To fully understand the environmental implications

of NMs use, knowledge regarding their mobility, bioavailability, and ecotoxicity is important (Farré et al., 2009).

Given the increase in NM use and the large fraction of waste placed in landfills worldwide, the probability of these products reaching municipal solid waste (MSW) landfills at the end of their useful life is high. Since nanotechnology is still in its early stages, there are currently no regulations pertaining to the disposal of NMs and their fate in MSW landfills is still unknown. Therefore, there is a need to study the fate and transport of NMs within waste environments and determine whether these products can potentially affect the environment as well as human health.

This research seeks to understand the fate of NMs within waste environments by examining the interactions between NMs and landfill leachate components. The primary focus of this thesis is the effect of Zinc Oxide (ZnO) on biological landfill processes, solids aggregation, and chemical speciation of Zinc (Zn) in landfill leachate following the addition of crystalline, nano-sized ZnO coated with triethoxycaprylylsilane. This research will (1) observe the effects of coated ZnO on five-day biochemical oxygen demand (BOD_5) and biochemical methane potential (BMP), (2) examine effects of solids aggregation on the fate of ZnO, (3) quantify the concentration of Zn by size fractions, and (4) model the chemical speciation of Zn in landfill leachate using Visual MINTEQ. ZnO was chosen as it is commonly found in personal care products which accounted for just over 55% of the inventory of NM-containing consumer products available in 2010 (Nanotech-Project, 2011). ZnO has been frequently used in sunscreens because at the nano-scale, ZnO can be transparent in the visible spectrum (390-750 nm) while retaining the ability to block UV rays (290-380 nm) (Linkov and Steevens, 2009; BASF, 2009).

Leachate treatment is a major expense for landfills and treatment options are variable depending on the final disposal options for the leachate (Vesilind et al., 2002). Biological treatment is widely used to reduce high concentrations of BOD_5 due to its dependability, simplicity, and cost-effectiveness (Renou et al., 2008). Inhibitory effects from NMs could impact the ability for the organisms to break down organic matter.

Inhibitory effects were tested using BOD_5 and BMP tests for aerobic and anaerobic processes, respectively. BOD_5 is used to determine the biodegradability of leachate generated within a landfill and also to estimate the capacity of landfill leachate to pollute streams and lakes if discharged untreated (Vesilind et al, 2002). Immediately after waste placement in a landfill the organic concentration (e.g. proteins, lipids, carbohydrates) in leachate will be high, therefore exhibiting a high oxygen demand (Akyurek, 1995). As a landfill matures there will be a decrease in leachable biodegradable organics within a landfill, reducing the oxygen required to breakdown the organic matter.

BMP is a method to determine the anaerobic biodegradability of organic compounds (ASTM E2170). The primary pathway for waste degradation within a landfill is through anaerobic processes (Versilind et al., 2002). Methanogens are responsible for the production of methane through the degradation of organics anaerobically. Heavy metals can be toxic to anaerobic organisms such as methanogens (Mosey et al., 1971). Understanding the effect of NMs through BMP studies will aide in understanding their effects on waste degradation processes and subsequent leachate treatment.

In this study, size fractionation is proposed to be used to determine the effects of ZnO on solids aggregation and the fate of Zn NPs added to leachate. Traditionally the main objective of size fractionation methods is to differentiate between colloidal and dissolved particles

(Wilkinson and Lead, 2007). A study conducted by Jensen and Christensen (1999) used an ultrafiltration method to size fractionate a leachate sample. In their study and in this study the dissolved fraction of particles was considered to be in the filtrate that passed through a 1.0-nm filter, while the particles in the fraction greater than 1.0 nm were considered colloidal.

Coupling data generated from size fractionation and leachate characterization, the chemical speciation of metals can be modeled using Visual MINTEQ, an equilibrium model that was developed based on USEPA MINTEQ2 (Gustafsson, 2000). Metal toxicity in aquatic systems has been extensively studied (Shaw et al., 2001, Ju-Nam et al., 2008, Baek et al., 2011), but the key challenge with these studies was the lack of information regarding the metal species that were responsible for toxicity. For example, a study by Li et al. (2011) determined that the toxicity of nano ZnO on Escherichia coli was due to Zn^{2+}.

Visual MINTEQ has been used extensively to study the mobility of metals in MSW landfills, during leachate treatment and in solidification/stabilization processing of hazardous sludge (Malviya and Chaudhary, 2006; Fernández-Olmo et al., 2007; Qu and He et al., 2008). In these studies, Visual MINTEQ was used to predict the species of metals leaching from hazardous materials, model the metal dissolution during leaching tests, and examine the influence of HA on the mobility of heavy metals in a landfill.

LITERATURE REVIEW

Municipal Solid Waste Landfills

Landfilling is a frequently utilized method of disposal in the US despite the push to replace landfills with recycling and combustion processes. In 2010, over 250 million tons of waste were generated in the United States, and of that 136 million tons were landfilled (USEPA, 2011). MSW is defined as having the following composition: mixed household waste, household hazardous waste (HHW), commercial waste, recyclables, yard waste, waste from community trash cans, bulky items, construction and demolition (C&D) debris (Vesilind et al, 2002).

Waste stabilization in a landfill is achieved through biological degradation. The overall waste stabilization process of a landfill occurs in four phases (Barlaz, 2002). In the first phase, oxygen present in the refuse after placement is depleted, during this time a large quantity of CO_2 is produced, there is an increase in the internal temperature, and the finally the system becomes anaerobic. In phase two, the hydrolytic bacteria's imbalanced activity begins to convert hemicellulose and cellulose into intermediates that are soluble. The methanogenic and acetogenic bacteria work in tandem to convert the soluble intermediates into CH_4 and CO_2. During this process short-chained carboxylic acids are produced leading to a decrease in pH, with minimal decomposition of solids. As the waste degradation process reaches the third phase methane production has begun due to the decrease in excess carboxylic acids. During this phase there is a noticeable decrease in leachate BOD_5 and chemical oxygen demand (COD), an increase in pH, and a substantial decomposition of hemicellulose and cellulose has begun. In the fourth and final stage of decomposition, the previous accumulation of carboxylic acid is consumed and methane production kinetics is now influenced by the rate in which hemicellulose and cellulose undergoes hydrolysis. The BOD/COD during this fourth stage is relatively low since the indigenous

microbial population will consume any dissolved organic matter that is biodegradable (Barlaz et al., 2002). In this phase, the BOD/COD is relatively low (<0.1) because any dissolved organics that are degradable have been consumed by the indigenous microbial population.

Landfill Leachate Quality and Treatment

Landfill leachate is a complex heterogeneous industrial wastewater that varies significantly from landfill to landfill and from time to time. This variation is due to influential factors such as composition and depth of solid waste, age of waste, precipitation rates, and landfill design and operations (Vesilind et al, 2002; Qasim, 1994, Viraraghavan and Singh, 1997, Kiely, 1997, Englehardt et al., 2006, USEPA, 1995). The concentration of leachate constituents peaks within the first two to three years of operation and slowly decreases as the landfill matures; this occurs as organics are removed through washout and waste degradation (Qasim, 1994, Maximova and Koumanova, 2006). Organics follow a decreasing trend over time, while it is observed that the inorganics concentration tends to vary due to adsorption, complexation, precipitation, and dissolution. This specific behavior is responsible for the mobilization or containment of heavy metals within a landfill.

The age of the landfill can be used to understand waste stabilization and provide information on the soluble components (organics) removed from a landfill (Qasim, 1994, Goi, et al, 2010). Young leachate is readily biodegradable due to the high BOD/COD ratio (>0.70), while a mature leachate (greater than ten years) has a low BOD/COD ratio (<0.1) (Ehrig and Stegmann, 1992, Kang et al., 2002, Englehardt et al., 2006, Tchobanoglous and Kreith, 2002). A leachate that falls between these two BOD/COD ratios in this study will be classified as middle aged. Typical characteristics of young leachate is a high BOD and COD concentration (1,000

mg/L-57,000 mg/L and 1500 mg/L-71,000 mg/L), low nitrogen concentration (<400 mg/L as N), and total suspended solids (TSS) concentration in the range of 200 mg/L-2,000 mg/L (Yilmaz et al., 2010, Qasim, 1994, Reinhart and Al-Yousfi, 1996, Kjeldsen et al., 2002). Mature leachate has a higher nitrogen concentration (> 400 mg/L as N), lower BOD and COD concentration (4-120 mg/L and 3-900 mg/L, respectively), and a reduced TSS concentration relative to young leachate (100 mg/L-400 mg/L) (Yilmaz et al., 2010). Additionally, the low molecular weight organics make up a larger fraction in young leachate, while the high molecular weight organics dominate the fraction of organics present in mature leachate (Englehardt et al., 2006).

Heavy metal concentrations in landfill leachate are influenced by pH, organic complexing agents such as fulvic and humic acids, and the presence of inorganic complexing/precipitating agents such as carbonates, hydroxides, and chlorides. Studies suggest that only a few heavy metals in leachate are present as free metal ions; but rather are primarily associated with organic colloidal fractions, but also some colloids that are inorganic in nature (Baun and Christensen, 2008). The metals most likely to be found associated with organic colloids are Cd, Cr, Cu, Pb, and Zn. Metals in leachate form stable complexes preferentially with high molecular weight organic components of older leachate (Calace et al, 2001; Christensen, 1996). The speciation of metals will have strong impact on which leachate treatment approaches are most effective (Baun and Christensen, 2008).

Leachate treatment is a major expense for landfills; treatment options vary depending on the final disposal options for the leachate (Vesilind et al., 2002). The challenge with leachate treatment is designing a process that can adapt to the fluctuations in leachate characteristics from day to day and as the landfill matures (Qasim, 1994, Lu et al., 1985). Treatment options for leachate include both on-site and off-site, including both biological treatment and

physical/chemical treatment (Lu et al., 1985). Off-site treatment involves discharging leachate to a domestic wastewater treatment facility but may require pretreatment prior to discharge (Qasim, 1994, Lu et al., 1985).

Biological treatment of leachate utilizes microorganisms to consume soluble and suspended biodegradable organic matter (Tchobanoglous et al., 2003, Qasim, 1994, Barber and Maris, 1984). Organics are removed aerobically through the use of oxygen to covert the organics to CO_2 and water, whereas anaerobic treatment is completed in the absence of oxygen and coverts organics to CH_4 and CO_2. Typical aerobic treatment technologies include activated sludge processes, aerobic sequencing batch reactors (SBRs), and aerated lagoons (Renou et al., 2008). Anaerobic treatment technologies include digesters and anaerobic SBRs which produce CH_4 that can be recovered to supplement energy requirements.

Physical and chemical treatment processes are primarily used to remove toxic compounds, color, and suspended solids, and are incorporated downstream of the biological process (Renou et al., 2008). As the age of the landfill increases there is a decrease in biodegradable organics which results in biological processes no longer being a feasible option for treatment (DeWalle and Chian, 1974). Coagulation-flocculation is used to remove recalcitrant organics by inducing flocculation and settlement of dissolved solids. As a result there is a large volume of sludge produced and potentially an increase in the heavy metal concentration in the liquid phase from the added coagulant (Amokrane et al., 1997, Renou et al., 2008, Tatsi et al., 2003). For example, chemical precipitation can be used as a pretreatment process to reduce the concentration of ammonia-nitrogen (precipitated as $MgNH_4PO_4 \cdot 6H_2O$) due to the negative effects it can have on the performance of the activated sludge processes (Renou et al., 2008, Li et al., 1999, 2001).

Membrane processes are now being used to treat landfill leachate and include ultrafiltration, nanofiltration, and reverse osmosis (Renou et al., 2008, Ushikoshi, 2002). Ultrafiltration removes macromolecules and particles and is used to study the molecular weight of organics in leachate. A study by Tabet (2002) found that ultrafiltration is not a primary option for treatment but it can be used as pretreatment prior to reverse osmosis. Large molecules can foul membranes commonly used in reverse osmosis thereby decreasing their efficiencies (Syzdek and Ahlert, 1984). Membrane bioreactors (MBRs) can achieve a high effluent quality with a high biomass concentration in compact design with a low sludge production (Renou et al., 2008, Ahmed and Lan, 2012, Bohdziewicz et al., 2008). Lastly nanofiltration can be used to meet multiple treatment needs removing both organics and inorganics but can also be impacted heavily by membrane fouling if it is not adequately controlled. Reverse osmosis is considered an efficient method for removing pollutants (98-99% rejection of COD and heavy metals) from leachate at both full and laboratory-scale (Linde et al., 1995, Bilstad et al., 1992). The major drawback to this treatment method, as well as other membrane processes, is membrane fouling which in turn increases operating costs to maintain the integrity of the membranes, as well as reducing the process efficiency (Renou et al., 2008).

Overall, biological treatment processes are best utilized to treat ammonia, COD, and heavy metals found in young leachate, while physical and chemical processes are best suited for the removal of recalcitrant organics in mature leachate (Renou et al., 2008, Ehrig and Stegmann, 1992). Given the increased regulatory discharge requirements for wastewater treatment, combined biological and physical/chemical methods are not sufficient to meet these stringent standards. Therefore membrane filtration is becoming an option to further reduce COD, inorganic, and particulate matter concentrations.

Nanomaterials

NMs have been key to the advancements in drug delivery and pharmaceuticals, cosmetics, foods, environmental remediation, nanotechnology, biomaterials, and energy production (Bhatt and Tripathi, 2011; Musee, 2011; Colvin 2003; Nyberg, Turco et al. 2008; Bittnar, Bartos et al. 2009; Sattler, 2011; Dreher 2004). These advancements can be attributed to the size dependent properties that both NPs and NMs exhibit due to their large surface area. Traditionally the properties of their bulk counterparts were dependent on their chemical composition and crystalline structure, and the surface atoms have negligible effect of the overall properties (Linkov and Steevens, 2009; Sattler, 2011).

Another attractive aspect of NPs is the ability to manipulate their functionality by synthesis method. The two main approaches for synthesising NPs are top-down and bottom-up. In the top-down method, NPs are produced from large uniform materials by using lithography and etching to produce the desired size, which can lead to surface imperfections (Baek et al., Mulvihill et al., 2009). The bottom-up approach is more widely used in the nanotechnology field. This approach builds NPs atom-by-atom by connecting individual monomers together (Cao, 2004). An advantage to this method is the ability to obtain a homogenous chemical composition and reduce surface imperfections.

The use of NPs in consumer products, manufacturing, and other technologies has increased due to their novel properties at the nano scale. The increased usage of NPs in cosmetic and personal care products results from the following characteristics: capability of absorbing UV light despite being transparent, more effective antioxidant in comparison to vitamin E, and antibacterial and anti-aging properties (Musee, 2011). Understanding the fate of coated NMs is challenging as the fate and transport of these materials will depend on the functionality of their

coatings as well as the chemical composition. For example, coatings can render a NM inert, limiting the toxicological or ecotoxicological effects, as long as the coating remains unchanged in environmental matrices (Musee, 2011).

Nanomaterials in the Environment

The interaction between NMs and the environment is not well understood, despite a plethora of information regarding the fate of natural NMs. Primary differences between engineered NMs and natural NMs at the nanoscale are the homogeneity of NMs as compared to the varying shapes, sizes and composition of natural NMs (Hood, 2004). Understanding the fate of NMs in the environment is based on their physcio-chemical properties (Bhatt and Tripathi, 2011). Due to the wide variety of NMs and their applications, their functionality will vary greatly, making it difficult to fully understand the fate of NMs in the environment. To determine the fate and behavior of NMs it is essential to know the chemical composition, mass and concentration, size distribution, specific surface area, surface charge/zeta potential, and the NM coatings (Klaine et al., 2008). Particle size is a strong driver that is responsible for the color and transparency, solubility, conductivity, and catalytic behavior properties that NMs can exhibit. The surface composition can also affect the properties of NMs, which includes optical properties, dispersability, catalytic behavior, and conductivity.

Various environmental conditions can also affect NM fate and transport such as ionic strength, salinity, pH, and organics concentration (Klaine et al., 2008). NMs tend to favor an aggregated form in aqueous solutions due to their interaction with natural organic matter (NOM) frequently found in natural systems. Furthermore, high molecular weight NOM compounds

enhance aggregation, while mobility is promoted by low molecular weight organics (Navarro et al., 2008).

In order to maintain the colloidal stability of NMs in cosmetic products, metallic NMs are coated with organic compounds to increase their hydrophobicity (Mafune et al., 2000). The potential interaction of NMs with pollutants (e.g. organic matter and heavy metals) is increased due to their shape and size, large surface area, tendency to aggregate, reactivity, and hydrophobicity (Musee, 2011).

The pathways for NMs to enter the environment include manufacturing, storage, distribution, and end of use disposal (Musee, 2011). Biswas and Wu (2005) summarized the sources, fate, and transport of NPs in the environment. More specifically these sources can be categorized by both point and non-point (Musee, 2011). Point sources include NM waste from manufacturing processes, sludge from wastewater treatment facilities, and MSW collection. Non-point sources include the direct usage of consumer product while swimming or bathing; which adds an additional challenge to understanding the ways in which NMs can enter the environment.

Understanding the properties of coated NMs is vital because the coating can reduce the NM bioavailability, in turn limiting the toxicological effects when NMs are present in the environment (Musee, 2011). If the coating is compromised, adverse effects can potentially be observed.

Application of ZnO Nanomaterials

ZnO has been extensively used in cosmetics, such as skincare products (Christian et al., 2008), but has other potential uses such as optoelectronic devices (e.g., laser diode and light-emitting diode), liquid crystal displays (Oh et al., 2006), transparent thin film transistors (Hoffmann et al., 2003), solar cells (Caputo et al., 2003), additive to rubber for car tires (Brown, 1976), and sunscreen lotion (Sattler, 2011). The extensive use of ZnO is attributed to the properties observed between the size of 20 nm to 100 nm, which include a high excitation binding energy (60 meV), large band gap energy of 3.36 eV, and dielectric constant (Sattler, 2011, Singh et al., 2007).

Nanomaterials in Landfills

NMs pose challenges to solid waste management as NMs enter the waste stream. It is uncertain whether traditional waste management practices are adequate to prevent NMs from entering the environment. Given the increase in NM use, the probability of these products reaching municipal solid waste (MSW) landfills at the end of their useful life is high. A study by Lecoanet et al. (2004) reported that NMs can display various transport properties within the environment. Therefore, solid waste management for NMs may require different waste management practices, which would vary depending on their respective properties. As stated, these properties vary depending on the synthesis process and applications.

Nanowaste is defined as a waste stream that contains NMs and their by-products, which are synthetic by nature and at the nanoscale (~1-100 nm). These waste products are produced during the manufacturing process, packaging and/or storage, and the introduction of consumer products containing NMs in the waste stream at the end of their useful life (Musee, 2011). The

waste materials produced during the manufacturing process may also be contaminated with NMs, which include personal protection equipment, industrial waste stream (biosolids production from treatment), and infrastructure used for manufacturing processes (e.g. pipes, tubing, etc.) (Musee, 2011). To adequately understand the potential introduction of NMs in the environment and the solid waste management field, a life-cycle assessment (LCA) must be conducted, which includes a cradle to grave analysis. Additionally the form NMs can take in each of their exposure pathways is vital to understand the fate and transport of these materials in the environment.

Summary

The current literature published pertaining to NMs outlines the increase utilization of these materials in consumer products and that it is inevitable that once NMs reach the end of their useful life they will be disposed of in a landfill. Despite the existing research on the fate of NMs in the environment, little information is available that can predict the fate of these materials in MSW landfills. The aforementioned studies reported information on the fate and transport of NMs under controlled conditions that do not adequately simulate conditions present in a MSW landfill. Therefore a study on the combined effects of a complex environmental matrix must be completed.

Currently the only publications available on the fate of NMs in landfills are review articles that focus on the life cycle assessment of these materials and the impact of nanosilver on methanogensis and biogas production from MSW (Yang et al., 2012). Therefore it is essential to study the fate and transport of NMs in landfills to ensure they are disposed of properly. Laboratory studies need to be completed to evaluate the mobility of NMs in the waste

environment, effect of NMs on landfills processes, and the changes in NM properties that could increase their bioavailability in the environment. All of these studies can provide information on the fate and transport of NMs in landfills.

METHODOLOGY

Studying the fate of coated ZnO NMs was accomplished by conducting four main tasks: collection and chemical characterization of landfill leachate, evaluation of the effects of NMs on landfill biological processes, size fractionation of leachate exposed to coated ZnO, and the chemical speciation of Zn modeled using Visual MINTEQ.

Collection and Chemical Characterization of Leachate Samples

Leachate was collected from two MSW (Class I) landfills in Central Florida. Leachate samples were collected directly from a lift station connected to an existing leachate collection system for a closed landfill cell. This location was ideal due to the known age of the cell which was initially determined, from historical data, to be a source of middle-aged (BOD/COD=0.1-0.7). Mature leachate was collected from a second landfill prior to an on-site aeration tank. This landfill was chosen because of the age of the landfill (operated since the 1960's); available historical leachate data confirmed the desired biodegradability of the leachate (BOD/COD<0.1). All samples were collected in clean high-density polyethylene (HDPE) containers and completely filled to eliminate headspace.

Leachate was characterized for pH, alkalinity, BOD_5, COD, conductivity, ammonia-nitrogen, and heavy metals following Standard Methods for the Examination of Water and Wastewater (APHA, 2005). Additionally, the dissolved HA concentration (filtered through a 450-nm filter) was determined by measuring absorbance using an UV-Vis spectrophotometer at 254 nm (Saito et al., 2003; Vermeer and Koopal, 1998).

Materials Used and Characterization

ZnO (Z-Cote HP1), coated with triethoxycaprylylsilane, was procured from BASF (Florham Park, New Jersey) and was selected based upon its extensive use in consumer products (Nanotech-Project, 2009). ZnO, as received, was characterized using High-Resolution Transmission Electron Microscopy (HRTEM) for morphology, crystallinity and particle size, and Dynamic Light Scattering (DLS) to measure average hydrodynamic diameter. Material characterization was completed by researchers at the University of Central Florida NanoScience Technology Center. The average particle size was 149 nm, which was determined from DLS and HRTEM analysis. Figure 1 shows the average particle distribution of ZnO.

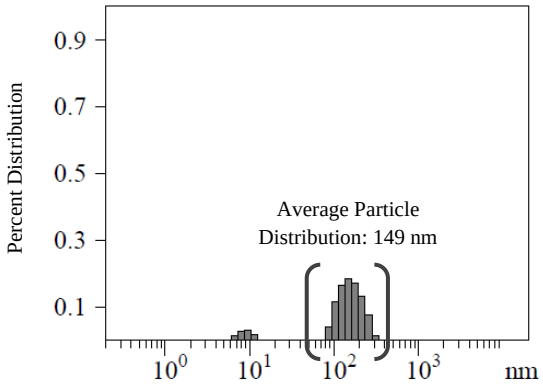

Figure 1. Average Hydrodynamic Radius of ZnO Prior to Leachate Addition

Leachate Exposed to Coated Zinc Oxide

Leachate was exposed to varying concentrations of coated ZnO to observe concentration-dependent effects on biological processes, solids aggregation, and dissociation. ZnO was added to reactors containing four L of leachate for a final concentration of 100 µg/L, 1.0 mg/L, and 100 mg/L of ZnO. Reactors were continuously stirred at room temperature (24ºC) for 60 days, as

shown in Figure 2. Results were compared to a control reactor treated in the identical manner without the addition of coated ZnO.

Figure 2. Continuously-Stirred Reactor

Effect of Coated ZnO on Biological Processes

The effect of NMs and their byproducts on both aerobic and anaerobic biological landfill processes was evaluated by performing BOD_5 and BMP tests. Aliquots of approximately 40 mL were removed over time from each reactor for BOD_5 and BMP tests.

BOD_5 was performed following standard methods 5120B (APHA, 2005). Dilution water was prepared using HACH Nutrient Buffer Pillows. A polyseed (International Laboratory Supply) obtained from Fisher Scientific was used to seed all samples. To eliminate oxygen consumption from nitrification (APHA, 2005), approximately 0.16 g of 2-chloro-6 (trichloromethyl) pyridine (TCMP) (nitrification inhibitor) were placed in each BOD bottle after the initial dissolved oxygen (DO) concentration was measured. Each bottle was incubated at 20°C for five days, after which the final DO concentration was determined.

The BMP was determined following ASTM method E2170. An anaerobic inoculum medium was prepared by combining anaerobically digested sludge obtained from a local domestic wastewater treatment facility and necessary nutrients that are required to sustain an anaerobic environment for 90 days. BMP assays were prepared individually in 125-mL serum bottles processed under anaerobic conditions (maintained through continuous nitrogen flushing). Serum bottles were filled with 5 to 15 mL of leachate after which the anaerobic inoculum was added, using a peristaltic pump for a final volume of 100 mL. All bottles were sealed with a rubber stopper and aluminum crimp, and incubated at 35±2 ^{o}C.

Gas quantity was determined using a frictionless syringe inserted into the stopper over a 30 to 90-day period until gas production ceased (<1 mL). Additionally the overall quality (i.e. carbon dioxide (CO_2) and methane (CH_4)) was measured using a Shimadzu – 14 gas chromatograph equipped with a TCD detector and Carboxen-1000 Column. During analysis the detector temperature was kept constant at 250°C, while the injection temperature was kept at 35°C for five minutes then ramped, in 20°C increments, up to 225°C over a 16-minute run time.

All results were compared to a control leachate sample that was treated in the identical manner, except without the addition of NMs. Any decrease in BOD_5 and BMP removal rates relative to control samples would suggest inhibitory effects.

Size Fractionation of Leachate Samples Exposed to Coated Zinc Oxide

Size fractionation was used to determine the effect of solids aggregation on the fate of ZnO and to quantify the concentration of Zn in each fraction. Aliquots of approximately 150 mL were taken from each reactor periodically over time using a wide-mouth pipette and under continuous stirring and fractionated, following which the mass of the solids in each fraction was measured.

The aliquots were filtered in series using a 1500-nm (Whatman 934-AH glass filter), 450-nm (nylon), 200-nm (nylon), and 1.0-nm filter (1000 NWML regenerated cellulose). The fraction greater than 1500 nm was determined by measuring the mass of the solids left on a 1500 nm glass filter after drying over-night at 105°C. Remaining fractions were measured by drying approximately 10-20 mL of filtrate in a pre-weighed beaker overnight at 180°C. Once drying was completed, beakers were cooled in a desiccator for 20 minutes and weighed. This method was also conducted for a control reactor that was treated in the identical manner, except without the addition of coated ZnO.

Metals Analysis of Leachate Exposed to 100 mg/L of Coated Zinc Oxide

The concentration of Zn in each size leachate fraction was quantified using Inductively Coupled Plasma-Optical Emission Spectrum (ICP-OES). The interaction of leachate constituents with coated ZnO could promote conditions where Zn dissociates from ZnO. The background concentration of Zn in leachate, as collected, was also determined before the addition of coated ZnO.

Aliquots of approximately 200 mL were pipetted from reactors under continuous stirring over time and fractionated. Filtrate was acidified with the addition of 2% nitric acid and stored at 4°C until analyzed. To reduce the interference of organic matter by ICP-OES during metals analysis, digestion was used to convert metals, which could be otherwise complexed with organic matter, to an unbound form that can be measured by ICP-OES (APHA, 2005). Acidified samples (10 mL to 20 mL) were transferred to and digested in 100-mL beakers. To reduce the loss of sample volume during digestion, all vials were rinsed with 0.05 N nitric acid and the liquid was added back to the aforementioned 100-mL beaker. Boiling chips and 10 mL of concentrated nitric acid were added to each beaker and contents were heated to a slow boil. Digestion continued with the addition of concentrated nitric acid as needed, until samples were light colored and clear. At this point, samples were cooled to room temperature before adding 10 mL of a 1:1 water/hydrochloric acid solution. Samples were heated for an additional 15 minutes, after which 2 mL of concentrated sulfuric acid were added and heating continued until brownish fumes were no longer evident. After digestion, samples were filtered using a 450-nm mixed cellulose ester membrane filter (filter differed from the initial fractionation (nylon) due to the increased pH from the digestion method) and diluted with distilled water to a final volume of 50 mL in a volumetric flask. Approximately 10 mL of each filtered sample were transferred to a 10-

mL conical vial for ICP-OES analysis. Duplicates and spikes were prepared to validate the accuracy of ICP-OES and confirm that the leachate matrix did not interfere with the ability to measure the dissolved metal concentration.

To evaluate the overall analytical performance of ICP-OES, usability of data, and the effect of the leachate matrix during analysis, both a duplicate and matrix spike were examined. One matrix spike and duplicate were prepared after every five to seven samples. The matrix spike was prepared by adding a known concentration of a metal standard directly to the leachate sample prior to acidification and digestion. The percent recovery was determined for each spike by comparing the added concentration to the measured concentration. Duplicates were prepared by taking, at random, a second aliquot of one of the test samples. Duplicate results were analyzed by comparing the average and standard deviation. Blanks (2% nitric acid) were placed periodically within the test setup to evaluate possible contamination which can cause results to be artificially high. Carryover was not an issue as the measured blank concentrations was consistently less than 0.0 mg/L. Matrix spike recoveries were above 92%, while duplicates percent differences were less than 10%. Detailed QA/QC results are summarized in Appendix D.

Due to the low solubility properties of coated ZnO and possibility of losses through pipetting and coating of glassware, a mass balance approach was used to ensure that the procedures accounted for ZnO in all fractions. Five identical beakers (containing 50 mg ZnO + 500 mL of leachate) were prepared and continuously stirred for seven days at room temperature (24°C). After seven days, 30 mL of leachate was pipetted, acidified and digested (following the same digestion method discussed previously). The remaining volume (470 mL) was acidified and digested, and a mass balance was calculated. Approximately 99% of the total mass of Zn

added was recovered when combining results from the 30-mL and 470-mL fractions. Of these fractions only 4% was recovered in the 30 mL aliquots, leaving the remaining 95% of Zn in the 470-mL sample. Appendix D provides a more detailed summary of the mass balance approach used to account for ZnO in all fractions. This method achieves a reasonable mass balance. Therefore we concluded that pipetting allowed us to measure the ZnO in the dissolved and suspended fraction of particles, which was the focus of our study but does not capture a representative amount of the non-aqueous phase which appears to be coating the reactors.

Chemical Speciation of Zinc using Visual MINTEQ

The chemical speciation of Zn in leachate is an important component in understanding the toxicity, mobility, and bioavailability of this metal in the environment. Visual MINTEQ, an equilibrium speciation model, was used to estimate the chemical species and equilibrium mass distribution of dissolved Zn found in leachate. The total Zn concentration in the fraction less than 1.0 nm, determined by metals analysis, was used as an input to a model of the chemical speciation of Zn. MINTEQ has the capability to estimate the binding of metal ions to multiple cations and ligands including organic matter which is assuming to be largely humic substances. The process to model humic acid complexation with Zn can be challenging because humic substances are heterogeneous and can have a large number of complexation sites (US EPA, 1999). Therefore, the Gaussian DOM model, which is integrated into Visual MINTEQ, was used to estimate the distribution of metal complexation sites with DOM (Allison et al., 1991) based upon the humic acid concentration, binding affinity, competition with other metal ions, and pH. The number of binding sites is estimated by assuming that the individual HA ligands contain a discrete number of binding sites (predominately carboxyl and phenolic hydroxyl groups (Purdue,

1980)). Numbers of binding sites are normally distributed with respect to the log *K* value for metal binding (Christensen et al., 1999, US. EPA, 1999), where *K* is a temperature-dependent equilibrium constant.

Visual MINTEQ input parameters used in this study included pH and concentrations of humic acid, Zn^{2+}, ammonia-nitrogen, alkalinity, sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), chloride (Cl^-), and nitrate (NO_3^-). All variables were assumed to be constant in concentration over time, except Zn^{2+} concentration. Average literature values were used for sulfate, phosphate, chloride, and nitrate concentrations for mature and middle-aged leachate, respectively. These values were included since these parameters were identified as ligands that can chelate dissolved Zn (Benjamin, 2002). Solid phase species concentrations were excluded from the model.

RESULTS AND DISCUSSION

Effect of Coated Zinc Oxide on Biological Processes

The fate of ZnO in leachate was studied using four different landfill leachates which represented different stages of waste degradation. From the leachate characteristics, summarized in Table 1, Leachates A, C, and D were classified as middle aged (BOD:COD=0.34-0.54), while B was found to be mature (BOD:COD=0.11). BOD_5, BMP, and solids were measured in Leachates A and B, while Zn concentration was determined in Leachates B-D.

Table 1. Leachate Characteristics

Parameters	Units	Leachate A	Leachate B	Leachate C	Leachate D
pH	S.U.	7.70	7.50	7.70	7.45
COD	mg/L	19,600	5,790	17,400	22,600
BOD	mg/L	10,500	618	5,850	9,080
BOD:COD	-	0.54	0.11	0.34	0.40
Ammonia-N	mg/L	1,890	546	1,633	1,360
Conductivity	µS/cm	23,800	6,570	19,900	N/A
Humic Acid Concentration	mg/L	N/A	310	6,470	6,500
Alkalinity	mg/L CaCO3	N/A	2,200	6,670	6,900
Total Solids	mg/L	15,200	5,350	14,900	13,950
Solids < 1500 nm	mg/L	14,320	5,290	14,800	13,700
Solids < 450 nm	mg/L	13,450	3,710	11,900	11,600
Solids < 200 nm	mg/L	13,430	3,670	11,700	8,540
Solids < 1.0 nm	mg/L	N/A	2,800	8,100	4,340

N/A: not available

The BOD_5, after exposure to ZnO, was analyzed to determine the rate of disappearance of biodegradable matter. BOD_5 results are summarized in Tables 2 and 3 for Leachates A and B, respectively. As shown in Figures 3 and 4, there was a significant removal of BOD_5 over time which may have been the result of the conversion of organic matter to CH_4 and CO_2 in the absence of oxygen. The rate of BOD_5 removal for both leachates followed first-order rate

kinetics. To determine the effects of ZnO on BOD_5, the first-order rate constants were calculated based on the first-order integrated rate law, as summarized in Table 4.

The differences between the control reactor and reactors with varying concentrations of ZnO were evaluated using the standard student t-test (two-tailed, $t_{0.05,1}=\pm 12.70$) for both individual BOD_5 results and first-order rate constants. Differences between the BOD_5 values and first-order rate constants were not statistically significant as the calculated student t-value for each reactor in comparison to the control fell within the hypothesis ($t_{0.05,1}=\pm 12.70$), suggesting that ZnO did not have any inhibitory effects on the ability for microorganisms to break down organic matter. The dilution factor range for Leachate A and B limited the ability to test inhibitory effects using dilutions; therefore in this study the inhibitory effect may have been diluted. On the other hand BOD5 disappearance is independent of dilution therefore the lack of inhibitory effects in this case was not affected by dilution.

Table 2. BOD_5 Results Over Time for Leachate A

	BOD_5 Concentration (mg/L)						
[ZnO]	Day 0	Day 16	Day 27	Day 42	Day 55	Day 74	Day 134
Control	9300	10,200	9,890	7,470	5,280	3,640	2,570
100 µg/L	9300	9,750	9,600	7,160	5,670	5,160	4,100
1.0 mg/L	9300	11,900	9,220	6,960	5,520	4,120	3,020
100 mg/L	9300	9,300	8,590	7,420	6,000	5,710	3,180

Table 3. BOD_5 Results Over Time for Leachate B

	BOD_5 Concentration (mg/L)				
[ZnO]	Day 0	Day 40	Day 60	Day 81	Day 102
Control	618	488	50	12	9.8
100 µg/L	618	581	63	12	4.4
1.0 mg/L	618	-*	185	9	7.8
100 mg/L	618	468	64	10	2.7

* Value was identified as an outlier at $\alpha=0.05$ since $P_{outlier}<0.05$.

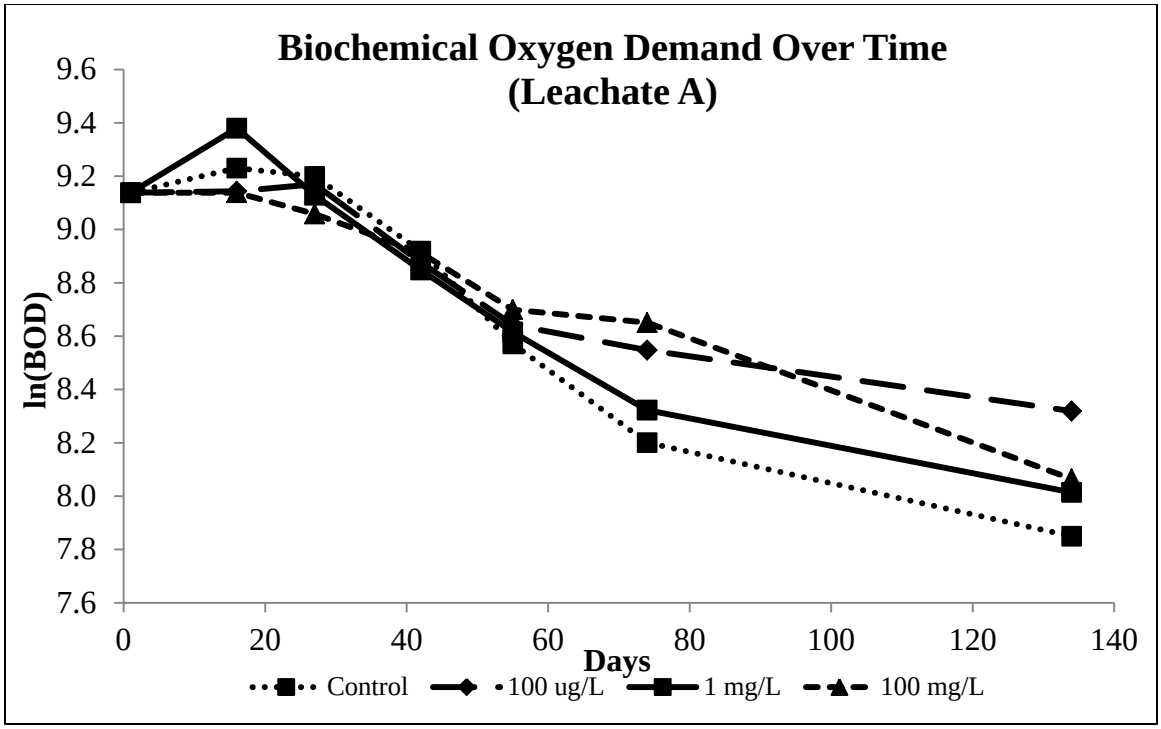

Figure 3. BOD_5 Over Time in Mature Leachate Exposed to ZnO

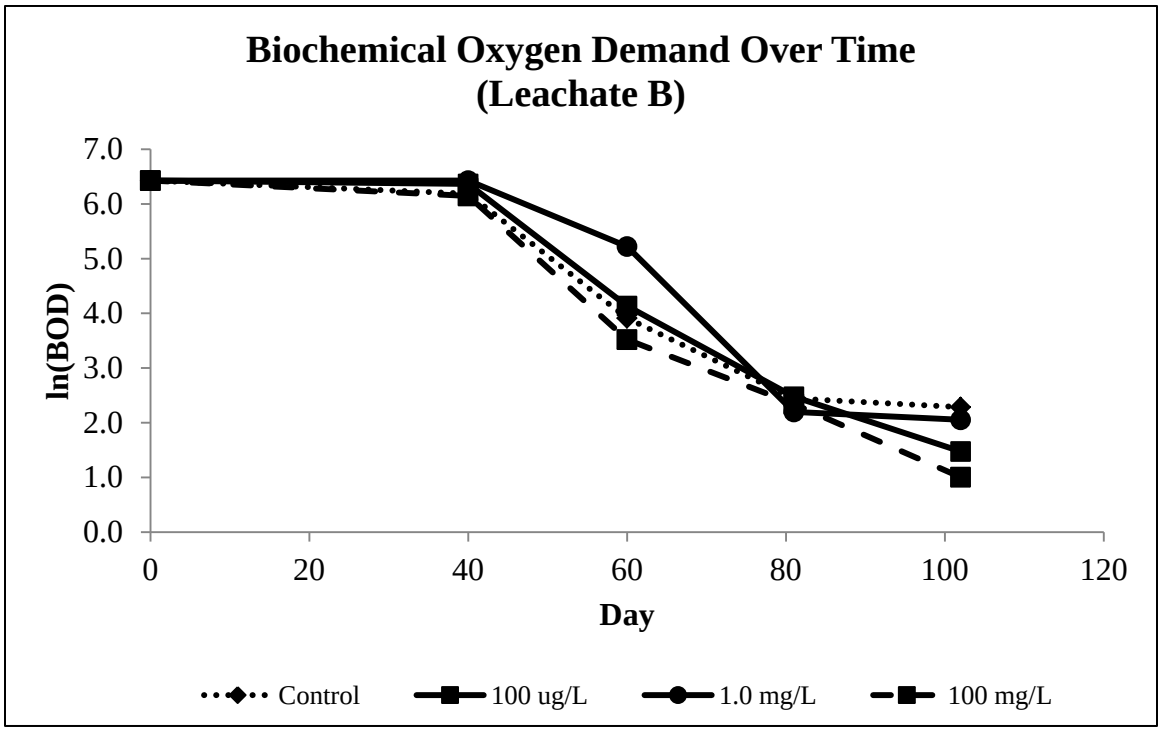

Figure 4. BOD_5 over Time in Mature Leachate Exposed to ZnO

Table 4. First-Order Rate Constants for BOD_5 Removal in Leachates A and B.

	First-Order Rate Constant (day^{-1})	
[ZnO]	Leachate A	Leachate B
Control	0.012	0.047
100 µg/L	0.0072	0.053
1.0 mg/L	0.010	0.046
100 mg/L	0.0085	0.057

The effect of ZnO on anaerobic biodegradability of organics present in leachate was studied using BMP tests. The cumulative gas production is shown in Tables 5 and 6, for Leachates A and B, respectively. The rate of gas production followed first-order rate kinetics, as seen in Figures 5 and 6.

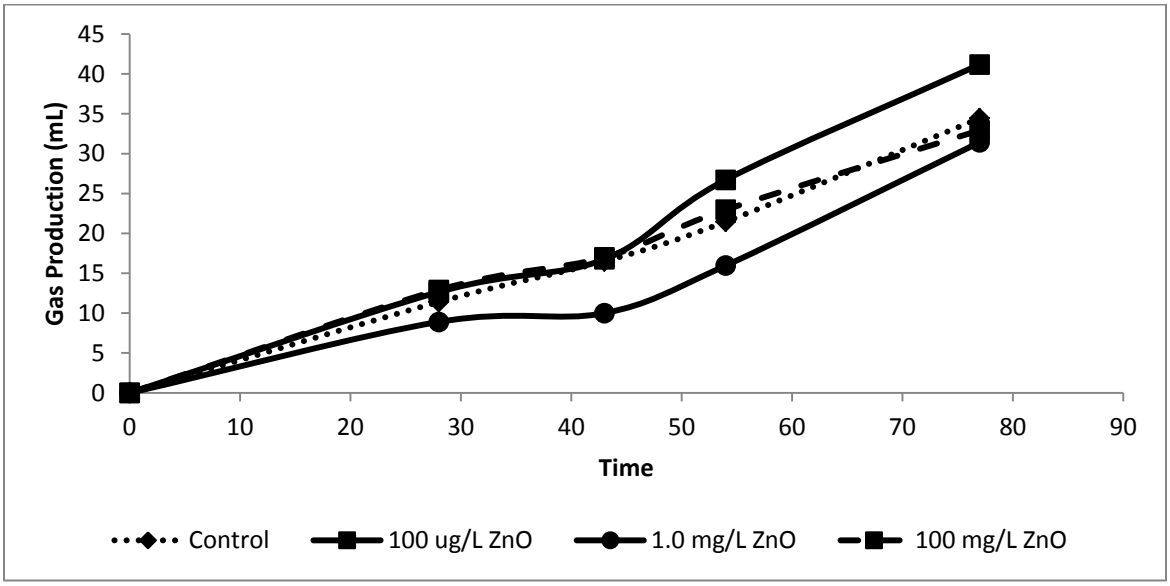

Figure 5. Cumulative Gas Production (mL) in Leachate A

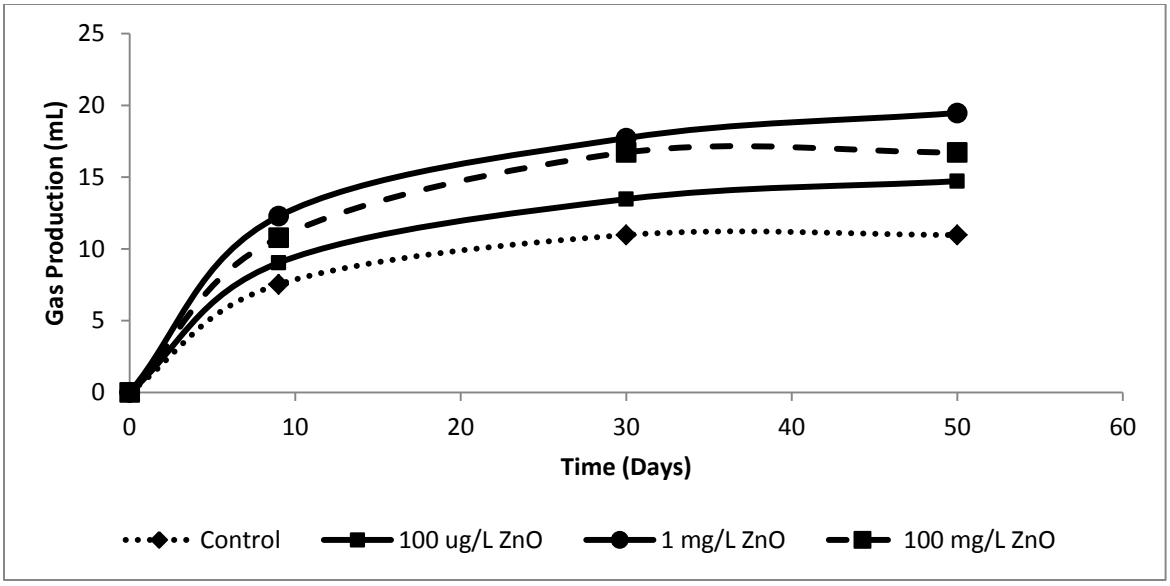

Figure 6. Cumulative Gas Production (mL) in Leachate B

Changes in gas quality can be an additional indicator of inhibitory effects on the removal of organics anaerobically, therefore CH_4 and CO_2 were measured. Tables 5 and 6 summarize the gas quality and quantity for Leachates A and B, respectively. The average gas composition for Leachate A was 64% CH_4 and 36% CO_2, while Leachate B had an average composition of 39% CH_4 and 61% CO_2. The CH_4 content (%) in Leachate A was expected to be greater than Leachate B due to its higher concentration of COD (19,600 mg/L and 5,790 mg/L, respectively) available to be converted anaerobically to CH_4 and CO_2.

Table 5. Gas Quality and Quantity of Leachate A

	Leachate A		
[ZnO]	CH_4 (% by volume)	CO_2 (% by volume)	Cumulative Gas Production (mL)
Control	62	38	47
100 µg/L	67	33	55
1.0 mg/L	59	41	46
100 mg/L	67	33	42

Table 6. Gas Quality and Quantity of Leachate B

	Leachate B		
[ZnO]	CH_4 (% by volume)	CO_2 (% by volume)	Cumulative Gas Production (mL)
Control	40	60	11
100 µg/L	39	61	15
1.0 mg/L	36	64	19
100 mg/L	41	59	17

Table 7. First-Order Rate Constants for Gas Production in Leachates A and B

	First-Order Rate Constant (day^{-1})	
[ZnO]	Leachate A	Leachate B
Control	0.023	0.019
100 µg/L	0.025	0.020
1.0 mg/L	0.027	0.018
100 mg/L	0.019	0.022

The differences between the control reactor and reactors with varying concentrations of ZnO were evaluated using the standard student t-test (two-tailed, $t_{0.05,1}=\pm 12.70$) for the calculated first-order rate kinetics. Differences between the first-order rate constants were not statistically significant, in comparison to the control reactor, as the calculated student t-value fell within the hypothesis ($t_{0.05,1}=\pm 12.70$), suggesting that ZnO did not have any inhibitory effects on the ability for microorganisms to break down organic matter in the absence of oxygen. The BMP results for Leachate B were actually higher for the reactors containing ZnO compared to the control reactor supporting the absence of inhibitory effects. The lack of toxicity in anaerobic digestion was also observed by Mu and Chen (2011) which reported that toxicity in anaerobic digestion was observed at concentrations of 11.6 mg/L and 17.6 mg/L of Zn^{2+} present due to the dissociation of ZnO NPs. Therefore, it can be concluded that ZnO, added to both middle aged

and mature leachate, does not have inhibitory effects on either aerobic or anaerobic processes. Appendix B summarizes the BOD and BMP results, detailed rate kinetic analysis and statistical data.

Solids Aggregation

Size fractionation was used to determine the effects of time and stirring on solids aggregation for Leachates A and B. It was observed that over a 60-day period there was an increase in the mass of particles greater than 1500 nm in both Leachates A and B, as seen in Figures 7 and 8. It was also noticeable that the higher concentrations of ZnO added to leachate showed the highest increase in the mass of particles present in the fraction greater than 1500 nm. The increase in this fraction can be attributed to continuous stirring. This increase in solids concentration may also be due to the effect of adding high concentrations NPs which has been observed by others (Buzea, et al., 2007).

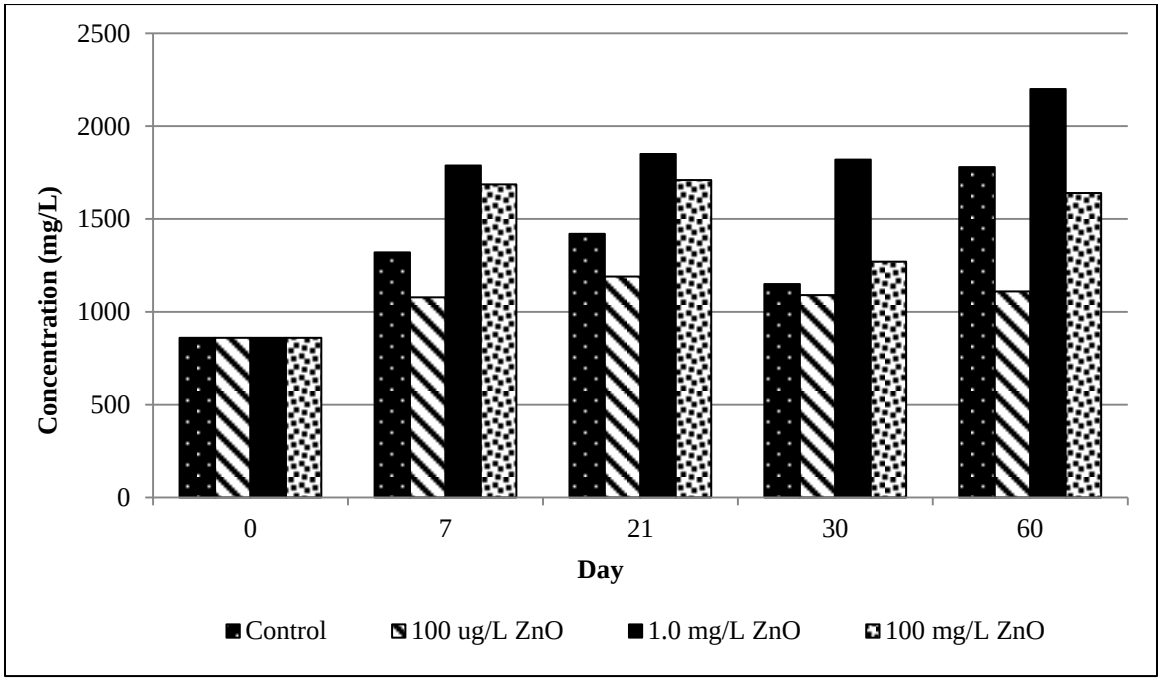

Figure 7. Particle Concentration Greater than 1500 nm Over Time (Leachate A)

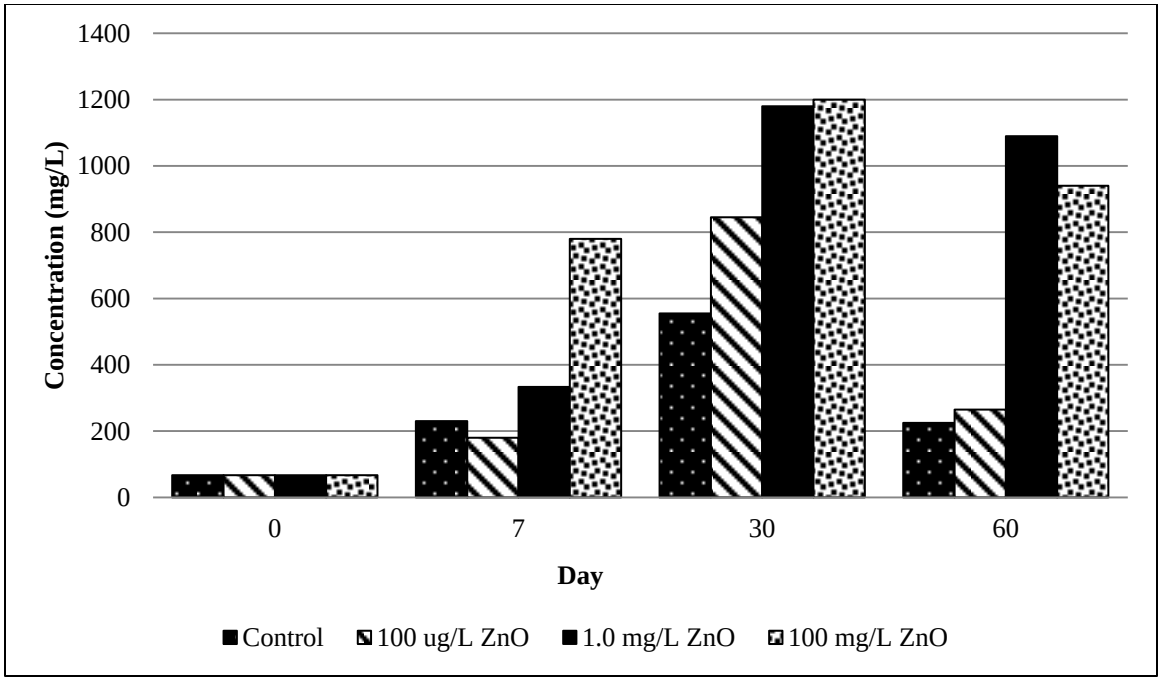

Figure 8. Particle Concentration Greater than 1500 nm Over Time (Leachate B)

Fate of Coated Zinc Oxide in Landfill Leachate

To study the fate of ZnO over time, a fractionation method was used to quantify Zn associated with different sized leachate fractions after exposure to leachate. In aqueous solutions metal oxides (e.g. ZnO) can agglomerate, dissolve, or be present as single non-aqueous particles (Stebounova et al., 2010). The state in which NMs are present in the environment will depend on the solution conditions including pH, ionic strength, and DOM (Stebounova et al., 2010, Chen and Elimelech, 2007, Hyung et al., 2007, Bian et al., 2011). These solution conditions in turn affect the dispersability, stability, aggregation, and potential for ZnO to dissolve in a leachate matrix.

The forms in which Zn can be present in leachate following ZnO addition and the origin of the Zn are outlined in Table 8. Zn found in the fraction not passing through a 1500-nm filter is considered to be non-aqueous due to the hydrophobicity of the added ZnO NPs. Zn present in the fraction between 200 nm and 1500 nm is considered to be dispersed ZnO NPs. Zn found in the fraction less than 1.0 nm is considered to be dissolved and either was present as background Zn or dissociated from the added ZnO NPs. Because ZnO NPs are greater than 10 nm, any additional Zn (beyond background) found in the dissolved fraction must have dissociated from ZnO NPs. Due to the ZnO hydrophobic coating, the particles were not initially dispersed in leachate, irrespective of the added concentration or leachate characteristics. The particles appeared to disperse within seven days after addition and ZnO was no longer visible on the surface.

Table 8. Defined Zinc Origin and Particle Suspended or Dissolved by Size Fraction

Size Fraction	State of Zn	Zn Origin
<1.0 nm	Dissolved	(I) Dissolved Background Zinc (II) Dissolved Zinc Dissociated from ZnO NPs
1.0 nm - 1500 nm	Suspended	(I) Zn Dissociated from ZnO NPs (II) Background Zinc
>1500 nm	Non-aqueous	(I) Insoluble ZnO NPs

The concentration of Zn by size fractionation after the addition of 100 mg/L of ZnO was completed over a 30-day period in mature and middle aged leachates (Leachates B-D). The results reported in Tables 9-11 for Day 0 are background control concentrations in the leachate, as collected. Tables 9-11 also summarize the total concentration of Zn in the three leachate fractions. The total Zn concentration added equalled approximately 81 mg/L. Total Zn measured was considerable less than this because of the solubility of ZnO and the tendency for ZnO to coat the sides the reactors, as shown in Tables 9-11.

Table 9. Concentration of Zinc (mg/L) by Size Fraction in Leachate B: BOD/COD:0.11*

Size Fraction	Day 0	Day 7	Day 30
<1.0 nm	0.34	0.73	1.11
<450 nm	0.38	1.23	3.22
<1500 nm	0.51	2.9	6.68

* Samples were not digested.

Table 10. Concentration of Zinc (mg/L) by Size Fraction in Leachate C: BOD/COD:0.34

Size Fraction	Day 0	Day 7	Day 30
<1.0 nm	0.25	0.029	0.068
<450 nm	0.27	0.18	0.21
<1500 nm	0.29	2.44	1.22

Table 11. Concentration of Zinc (mg/L) by Size Fraction in Leachate D: BOD/COD: 0.40

Size Fraction	Day 0	Day 7	Day 30
<1.0 nm	0.39	0.48	0.33
<450 nm	0.66	1.50	0.72
<1500 nm	0.66	3.48	3.77

To better observe the cumulative Zn concentration in each fraction over time the concentration of Zn in the three leachate fractions was plotted in Figures 9-10. There was an increase in the concentration of Zn present in fraction between 450 nm and 1500 nm. Christensen et al. (1998) discusses the potential for heavy metals in landfills to leach out of waste materials depending, in part on the complexing capacity of organic materials commonly leaching from organic MSW. It has been reported that the presence of DOM increases the stability of both hydrophilic and hydrophobic NMs (Chen and Elimelech, 2007, Bian et al., 2011, Stebounova et al., 2010, Hyung et al., 2007, Aiken et al., 2011). Therefore, Zn species found in the fraction greater than 1.0 nm may be (1) ZnO associated with HA or other DOM, (2) ZnO complexed with other inorganic leachate components, (3) dispersed ZnO NPs, or (4) Zn from background or dissociated ZnO. The increase of Zn in the larger fractions in all samples over the background can be attributed to leachate components that have interacted with the ZnO coating, which promoted ZnO dispersion, and to the changing wetting properties of ZnO due to the direct interaction with humic and fulvic acids.

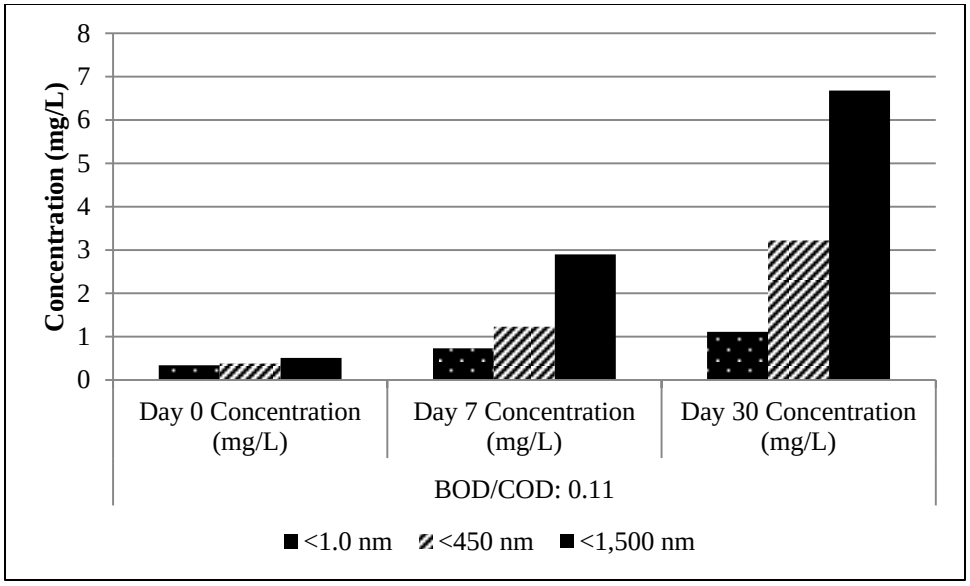

Figure 9. Cumulative Concentration (mg/L) of Zinc by Size Fraction (Leachate B)

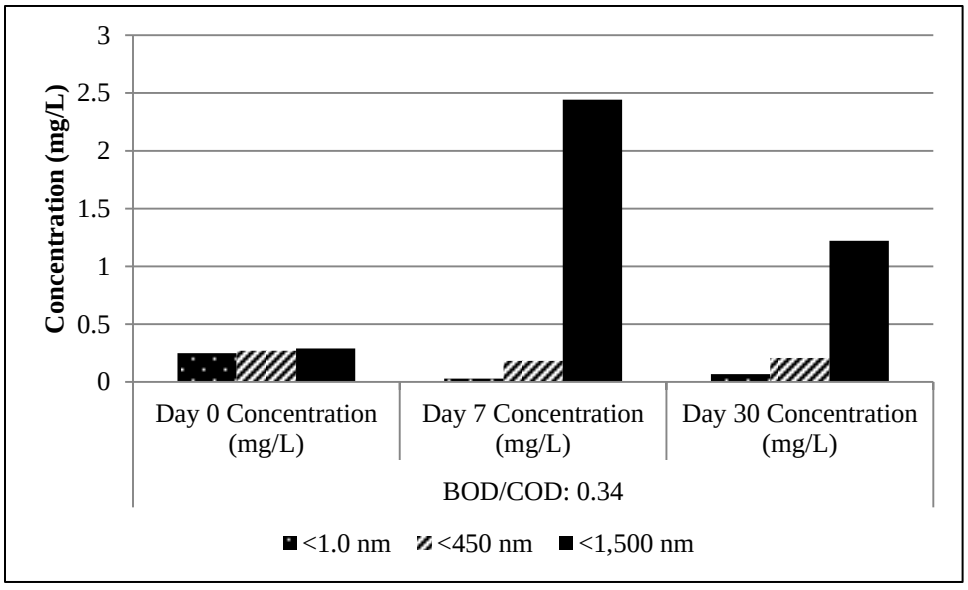

Figure 10. Cumulative Concentration (mg/L) of Zinc by Size Fraction (Leachate C)

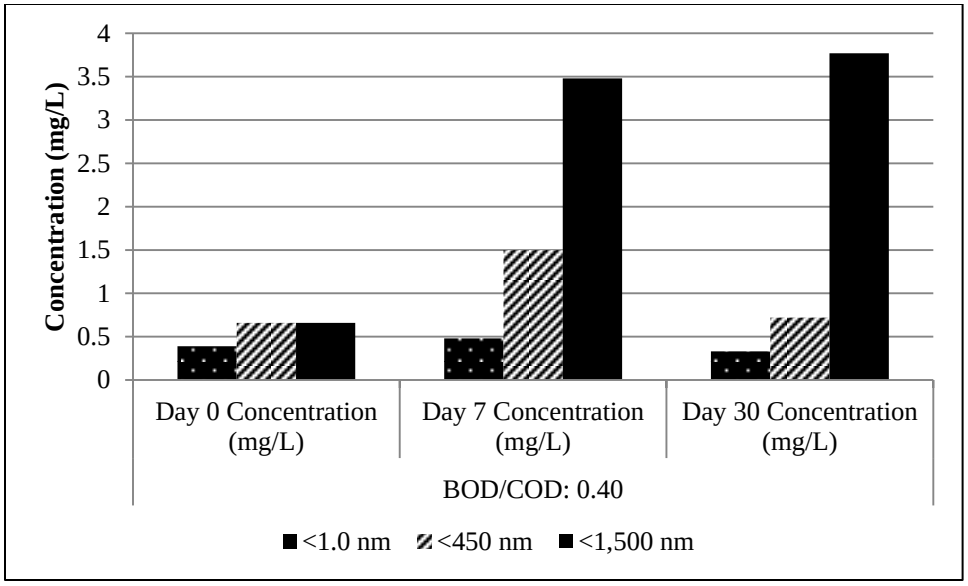

Figure 11. Cumulative Concentration (mg/L) of Zinc by Size Fraction (Leachate D)

As shown in Figure 9, there was an increase in the dissolved fraction of Zn in Leachate B over time, although Zn was predominantly found in the larger fractions. Humic material consists of two domains: hydrophobic (aromatic-rich) and hydrophilic (containing carboxylate, hydroxyl and amide groups). Humic matter-nanoparticle interaction may involve the hydrophobic domain of the humic matter interfacing with the hydrophobic silica coating of ZnO. Over time, the hydrophilic domain can penetrate the silica coating and facilitate Zn diffusion out of the particle.

The dissolved fractions present in Leachates C and D were either unchanged or declined, as shown in Figures 10 and 11. The different behavior of Zn in Leachates C and D relative to Leachate B (significant increase in Zn <1.0 nm) can be attributed to the differences in the dissolved solids (4340 mg/L-8100 mg/L and 2800 mg/L, respectively) and ionic strength (19900 µS/cm and 6570 µS/cm, respectively). The ionic strength may affect the stability of ZnO NPs within the leachate matrix. Stability of NMs within an aqueous environment is due to the repulsive forces between the charged NP surface and the liquid matrix (Bian et al., 2011). High

ionic strength of leachate compresses the surrounding electrical double layer (EDL), decreasing the repulsive barrier of HA/ZnO particles, and agglomeration occurs (Bian et al., 2011, Zhang et al., 2009, Jiang et al., 2009).

When solid particles have a propensity to agglomerate due to changes in the EDL there is a decline in the interfacial area that is available to undergo dissolution/dissociation of particle components (Mehra et al., 2001). The extent of particle to agglomerate is dependent on the degree of compression of the EDL. This increase in particle agglomeration will allow larger particles to settle to the bottom of the reactor, even under continuous stirring (Paul et al., 2004). The settle solids decrease the interfacial area and mass transfer coefficient of the particles, hindering the potential for Zn to leach from ZnO particles.

Speciation of Zinc in Landfill Leachate

The chemical speciation of Zn in Leachates B-D was modeled using input values summarized in Tables 12 and 13. The input values yielded chemical speciation data that were used to determine the form in which Zn takes in leachate and the percentage of Zn present as Zn^{2+}. The chemical species present in leachate upon the dissociation of coated ZnO are summarized in Equation 1.

Table 12. Visual MINTEQ Leachate Inputs

Parameters	Units	Leachate B	Leachate C	Leachate D
pH	S.U.	7.52	7.7	7.45
Ammonia-N	mg/L	546	1633	1360
Humic Acid	mg/L	310	6,470	6,500
Alkalinity	mg/L CaCO3	2,200	6,670	6,900
Temperature	°C	24	24	24
Sulfate[1]	mg/L	50	75	75
Phosphate[1]	mg/L as P	2.5	2.5	2.5
Nitrate[2]	mg/L	10	25	25
Chloride[1]	mg/L	100	4000	400

1 Qasim et al., 1994
2 Historical leachate quality data from landfill

Table 13. Concentration of Zinc (mg/L) in the Fraction Less Than 1.0 nm

	BOD/COD	Day 0	Day 7	Day 30
Leachate B	0.11	0.34	0.73	1.10
Leachate C	0.34	0.25	0.029	0.068
Leachate D	0.40	0.39	0.48	0.33

$$C_{T,Zn} = Zn^{2+} + ZnHCO_3^+ + Zn(CO_3)_2^{-2} + ZnDOM + ZnOH^+ + Zn(OH)_2(aq) + Zn(NH_3)_2^{2+} + ZnNH_3^{2+} + ZnCO_3(aq) + ZnCl^+ + ZnSO_4(aq) + ZnPO_4(aq) + Zn(NH_3)_3^{+2} + Zn(NH_3)_4^{+2} + Zn)(OH)_3^- + Zn(OH)_4^{-2} + Zn(SO_4)_2^{-2} + ZnCl_2(aq) + ZnCl_3^- + ZnCl_4^{-2} \quad (1)$$

The chemical speciation of Zn in leachate is important because toxicity, physical and chemical properties, and bioavailability are all related to the chemical form it takes (Li et al., 2010). Table 14 summarizes the predominant Zn species present in Leachates B-D on Day 30. Zn is predominately associated with DOM (e.g. humic acid), carbonate ($ZnCO_3$ (*aq*), and $Zn(CO_3)_2^{2-}$) and bicarbonate ($ZnHCO_3^+$), and also present as free ionic (Zn^{2+}). The remaining species shown in Equation 1 make up less than 2.0% of the total concentration of dissolved Zn. Figures 12-14 summarizes the complete chemical speciation of Zn in the fraction less than 1.0 nm for both middle-aged (Leachates C-D) and mature leachates (Leachate B) over time.

Table 14. Predominant Dissolved Zinc Species in Leachates B-D on Day 30 (% by weight)

	Leachate B	Leachate C	Leachate D
	Day 30	Day 30	Day 30
Zn DOM	97.2	99.5	99.6
$ZnCO_3$ (aq)	1.2	0.25	0.18
$ZnHCO_3^+$	0.53	0.08	0.10
$Zn(CO_3)_2^{2-}$	0.05	0.06	0.03
Zn^{2+}	0.86	0.06	0.07

Less than 1% of the dissolved Zn present in Leachates B-D was present as Zn^{2+}. Dissolved Zn^{2+} in the environment has been identified to be toxic, as opposed to ZnO, provided it is bioavailable. ZnO NP toxicity has been observed in Escherichia coli, and endogenous

respiration and BOD biodegradation in wastewater treatment, at concentrations between 500 mg/L and 800 mg/L (Li et al., 2011, Liu and Wang, 2011). Additionally, Mu and Chen (2011) reported that toxicity in anaerobic digestion was observed at concentrations of 11.6 mg/L and 17.6 mg/L of Zn^{2+}. The Zn^{2+} concentrations quantified in this study were significantly lower in comparision to the referenced studies which supports the lack of inhibitory effects observed in BOD_5 and BMP. Yan et al. (2011) also observed low toxicity of ZnO NPs (>100 mM) in gram-positive bacteria and reported that the crystalline structure was not damaged after exposure. HRTEM images show the crystalline core structure of ZnO intact after exposure to Leachate A for 95 days (Figure 15), supporting the resistance of ZnO NP to dissociate in leachate. It was also observed in a study by Huang et al. (2008) that the greatest cellular damage (S. agalactiae and S. aureus) was observed when there was a substaintial change in the crystalline structure of ZnO NPs. This suggests that the lack of inhibitory effect can also be supported by the intact crystalline structure of ZnO in Leachate A.

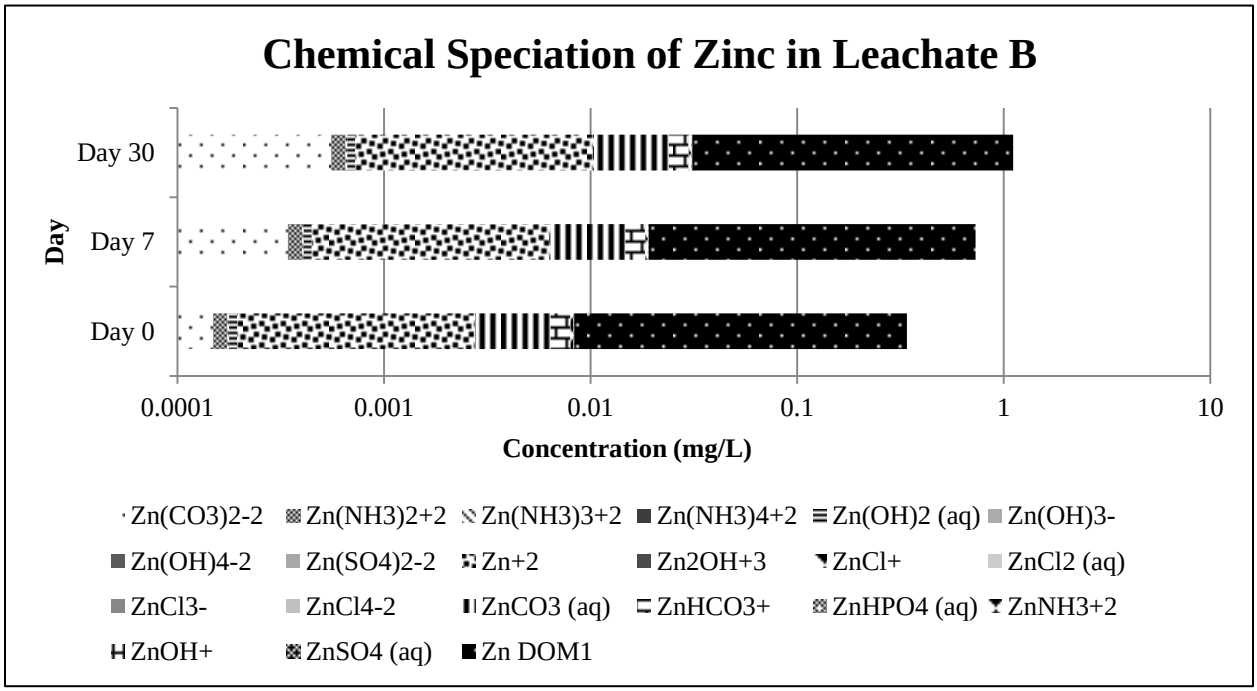

Figure 12. Chemical Speciation of Dissolved Zinc in Leachate B (BOD/COD: 0.11)

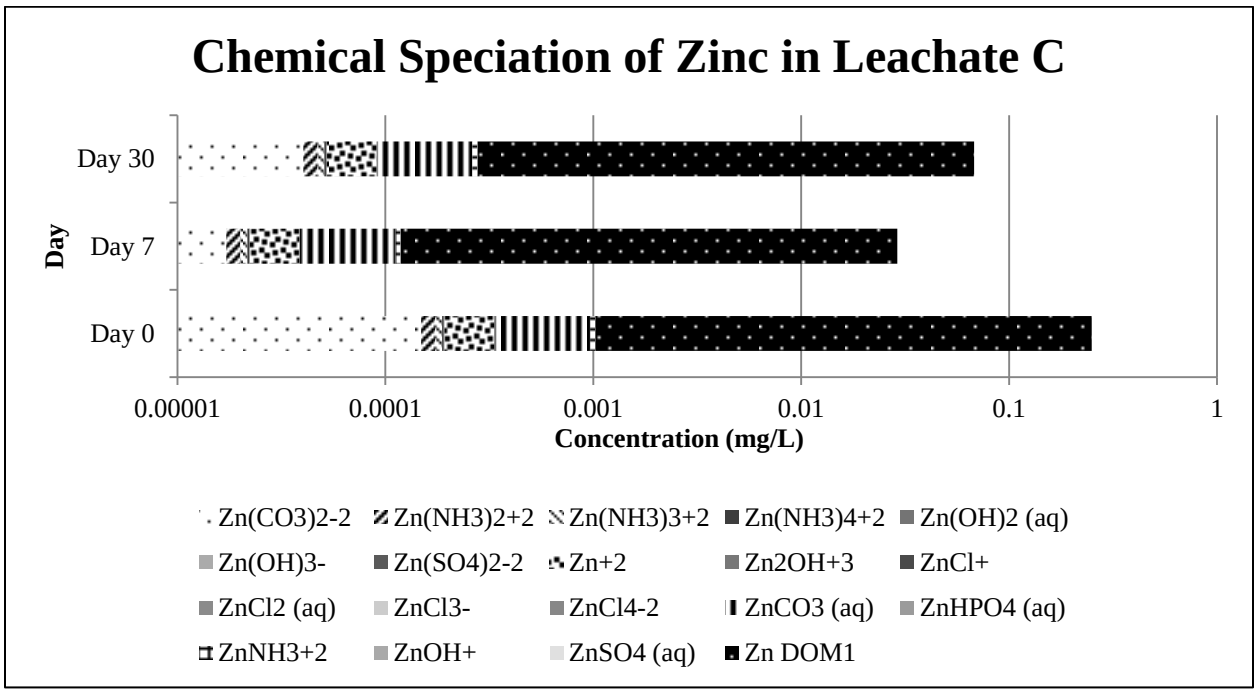

Figure 13. Chemical Speciation of Dissolved Zinc in Leachate C (BOD/COD: 0.34)

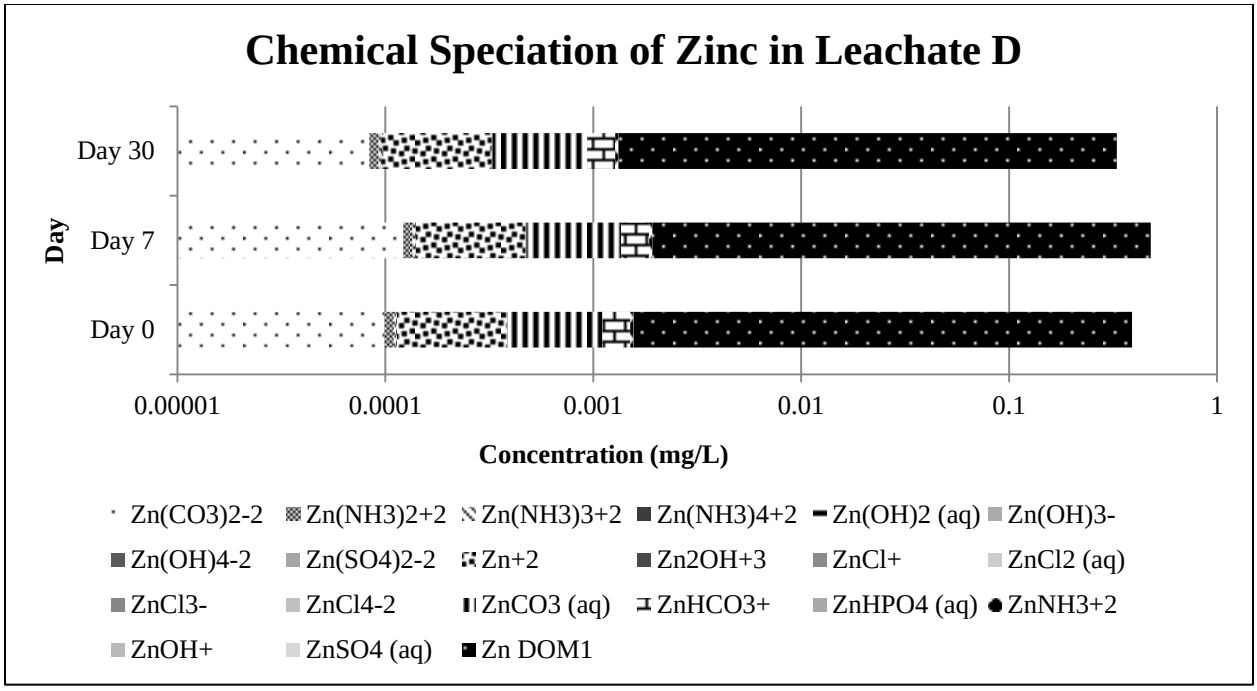

Figure 14. Chemical Speciation of Dissolved Zinc in Leachate D (BOD/COD: 0.40)

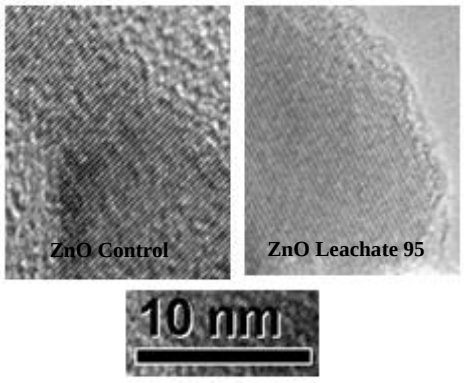

Figure 15. Crystalline structure of ZnO as received and after 95 days of exposure to Leachate A

CONCLUSIONS

The dissociation of coated ZnO NMs exposed to mature leachate (Leachate B) occurred over a 30-day period, while the dissolved fraction in middle aged leachate (Leachate C and D) decreased or remained unchanged. It was observed that the relatively high dissolved solids concentration (less than 1.0 nm) and ionic strength in Leachate A and B promoted solids aggregation, potentially decreasing the propensity for ZnO NMs to dissociate. However, the increase in dissolved Zn in Leachate B was minimal in comparison to the total ZnO added. Insight into the mobility of ZnO within the landfill environment was gained from the substantial change in the cumulative concentration of Zn in the fraction less than 1500 nm. This increase is attributed to dispersion of ZnO due to interaction with DOM, stabilizing the ZnO particle in an aqueous solution. Dispersability suggests that NMs will become mobile within the landfill environment, assuming the NMs have leached from the consumer products. Once mobile, ZnO particles were destabilized (compression of EDL) by the high concentration of ions present in leachate leading to the aggregation of particles. The potential for ZnO to dissociate may have been hindered by solids aggregation due to higher ionic strength in Leachates C and D, whereas in Leachate B dissociation may have occurred due to the lower concentration of large particles. Strong aggregation increases particle size and mass and promotes settling out of solution, reducing particle surface area and therefore hindering the potential for dissociation. ZnO did not inhibit anaerobic or aerobic processes in either middle aged or mature leachate, presumably due to the low concentration of dissolved ionic Zn. The primary chemical species was ZnDOM, which was over 97% of the total dissolved Zn in both mature and middle aged leachates; less than 1% was in the ionic form of Zn^{2+} in middle aged and mature leachate.

Fractionation, BOD_5 and BMP tests, and chemical speciation modeling provided insight into the mobility of ZnO in landfills and the absence of inhibitory effects on landfill processes. Aggregation of ZnO NPs may prevent movement through traditional containment systems (i.e. geomembrane liners) due to the increased particle size. However, the increased dispersion suggests that ZnO NPs will be transported out of the landfill in the leachate. Nevertheless it was found that biological treatment of leachate should be unaffected by the presence of ZnO. The bioavailability of Zn was not substantially affected by the presence of ZnO due to affinity of dissolved Zn for DOM. However, due to the heterogeneity of landfill leachate and the utilization of different NM coatings, it is challenging to predict the overall mobility of other NMs in a landfill.

Overall the understanding of the fate of coated ZnO NMs and their behavior in landfill leachate will directly benefit landfill operations and leachate management. Research data can aide regulatory agencies in addressing potential nanotoxicological issues and develop a knowledge base to enhance the understanding of the fate and transport of NMs in landfills. Such understanding will ensure that these materials are properly managed from cradle to grave, while protecting human health and the environment.

RECOMMENDATIONS

This research addresses specific questions pertaining to the impact of coated ZnO on biological landfill processes and leachate treatment. It brought to light additional knowledge gaps that remain unanswered regarding the fate of NMs in landfills. These knowledge gaps pertain mainly to the lack of analytical techniques that can identify NMs in a complex heterogeneous matrix; variations in NM coating, size, and shape; and the mechanisms responsible for the dissociation of NMs.

Once NMs enter a landfill it is challenging to track its mobility and behavior in such a complex and constantly changing environment. It was observed through this study that it was not possible to identify the exact forms and in which size fractions of leachate ZnO was present. There are also limitations to the ability to use existing imaging techniques to capture the changes in NM characteristics within complex environmental samples. It was observed that DOM and solids hindered the ability to easily locate and identify NMs using HRTEM. The following research recommendations have been developed based on this study and a literature review.

- As the number of consumer products containing NMs continue to increase it is important to evaluate the potential pathways for NMs to reach landfills at the end of their useful life and their quantity. A LCA is recommended to map out both the indirect and direct pathways and the form in which NMs will be present within the waste stream (e.g. single NP or NPs complexed with DOM). A direct pathway includes disposal in municipal solid waste (MSW) landfills, whereas indirect pathway include industrial and domestic wastewater treatment (through the production of sludge). The challenge with this recommended study is the lack of information provided by manufacturers on the concentration of NMs present in consumer

products. This information is essential to adequately develop a mass loading rate of NMs for each identified pathway.

- Due to the unavoidable reality that NM-containing products (nanowaste) will be present in MSW landfills it will be imperative to determine the potential for NMs to leach out of consumer products after disposal. Based on this study it was observed that ZnO behaved differently in different leachates with respect to dissociation, suggesting that NM leaching behavior depends on landfill conditions. Therefore it is advisable that the leachability be tested in a matrix that represents the changing conditions as a landfill matures. A modified Toxicity Characteristic Leaching Procedure (TCLP) can be used to determine the leachable NMs and heavy metals (assuming dissociation) from consumer products. Extraction fluids can be used from the existing TCLP method to simulate landfill conditions. It is suggested that the filter size (450 nm) be decreased to 200 nm given the average size of NMs is less than 200 nm. This would allow for dissolved metals or NMs to be filtered from the liquid extract. This method can provide information on the potential for NMs to become mobile in leachate or if NMs will remain within their respective consumer products.
- Once NMs become mobile within a landfill or the environment their behavior will be altered by the surrounding aqueous matrix. Most studies have attempted to simulate realistic environmental conditions but have exposed NMs to an aqueous matrix with limited number of components, (e.g. humic acid and ionic strength). A more detailed study on the fate of NMs exposed to a more realistic environment will provide insight on their fate and mobility. It is proposed that the individual and combined effects of varying concentration of DOM, total solids, ionic strength, and ligands be used to

study the aggregation and mobility properties of NMs. It is predicted that this study could lead to identifying a dominant component responsible for the aggregation or mobility of NMs. This dominant component could be used as a primary indicator of the fate and transport of NMs.

- The potential for ZnO NPs to be removed during leachate mixing was observed. Since there were no effects on aerobic or anaerobic processes there will be no effects on traditional landfill biological processes and leachate treatment biologically. On the other hand there was an increase in the fraction of particles greater than 1500 nm, which suggests that physical/chemical processes can be implemented to remove these particles. If membrane processes are part of an existing treatment system there would be concerns that there would an increased rate of fouling reducing the overall treatment efficiency and effluent quality. Sedimentation can be another option if the particle settling velocity falls within the existing sedimentation basin design. Therefore it is recommended that chemical/physical processes and/or membrane filtration be used to remove NPs from the wastewater stream.
- Lastly, it is recommended that regulations be implemented to ensure safe disposal and manufacturing of NMs. Unfortunately due to the lack of consumer product composition, particularly pertaining to the NM concentration, coating, and size, it will be difficult to implement regulations that would be applicable to all NMs. This study provided insight on the fate of coated ZnO in landfills but this behavior can vary greatly simply due to composition and coating for each NM. In order to develop regulations, it will be important to determine a key parameter that could predict mobility in the environment based solely on the characteristics that can be provided

by a manufacturer (hydrophilic/hydrophobic, coating composition, and size). Overall the development of such regulations will be challenging and will not be possible unless there is more detailed knowledge of the fate and transport of NMs in MSW landfills, as well as the environment.

APPENDIX A: LEACHATE CHARACTERISTICS

Table A-1. Leachate A Characteristics

Parameters	Results	Units
pH	7.765	S.U.
COD	19613	mg/L
BOD	10515	mg/L
BOD:COD	0.54	
Ammonia-N	1890	mg/L
Conductivity	23800	uS/cm
Solids Concentration		
X>1.5 um	860	mg/L
X<1.5 um	14300	mg/L
X<0.45 um	13500	mg/L
X<0.20 um	13400	mg/L
X<0.001 um	-	mg/L

Table A-2. Leachate B Characteristics

Parameters	Results	Units
pH	7.52	S.U.
COD	5790	mg/L
BOD	618	mg/L
BOD:COD	0.11	
Ammonia-N	546	mg/L
Conductivity	6569	uS/cm
Solids Concentration		
X>1.5 um	67	mg/L
X<1.5 um	5285	mg/L
X<0.45 um	3525	mg/L
X<0.20 um	3665	mg/L
X<0.001 um	2800	mg/L

Table A-3. Leachate C Characteristics

Parameters	Results	Units
pH	7.7	S.U.
COD	17400	mg/L
BOD	5850	mg/L
BOD:COD	0.34	
Ammonia-N	1633	mg/L
Conductivity	19875	uS/cm
Alkalinity	6670	mg/L CaCO3
Solids Concentration		
X>1.5 um	110	mg/L
X<1.5 um	14810	mg/L
X<0.45 um	11890	mg/L
X<0.20 um	11680	mg/L
X<0.001 um	8100	mg/L

Table A-4. Leachate C Characteristics

Parameters	Results	Units
pH	7.45	S.U.
COD	22600	mg/L
BOD	9075	mg/L
BOD:COD	0.40	
Ammonia-N	1360	mg/L
Alkalinity	6500	mg/L CaCO3
Solids Concentration		
X>1.5 um	250	mg/L
X<1.5 um	13700	mg/L
X<0.45 um	11600	mg/L
X<0.20 um	8540	mg/L
X<0.001 um	4340	mg/L

APPENDIX B: BIOCHEMICAL OXYGEN DEMAND AND BIOCHEMICAL METHANE POTENTIAL

Five-Day Biochemical Oxygen Demand Concentration (mg/L) Summary

Table B-1. BOD_5 (mg/L) of Leachate A on Day 1

	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	Average	Standard Deviation
Leachate	8700	9600	9600	9300	520

Table B-2. BOD_5 (mg/L) of Leachate A on Day 16

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	Average	Standard Deviation
Control	10500	10200	9900	10200	300
100 µg/L	9300	10200	N/A	9750	636
1.0 mg/L	13800	13200	8550	11850	2870
100 mg/L	10200	8700	9000	9300	794

Table B-3. BOD_5 (mg/L) of Leachate A on Day 27

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	Average	Standard Deviation
Control	10890	10020	8760	9890	1071
100 µg/L	9360	10530	8910	9600	836
1.0 mg/L	9420	9810	8415	9215	720
100 mg/L	8640	9180	7950	8590	617

Table B-4. BOD_5 (mg/L) of Leachate A on Day 42

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	BOD Bottle #4	Average	Standard Deviation
Control	7290	7800	8640	6165	7474	1035
100 µg/L	7560	8040	6825	6210	7159	806
1.0 mg/L	7890	7410	6375	6172.5	6962	823
100 mg/L	7440	9120	7035	6090	7421	1266

Table B-5. BOD_5 (mg/L) of Leachate A on Day 55

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	Average	Standard Deviation
Control	5130	5220	5475	5275	179
100 µg/L	6360	5295	5340	5665	602
1.0 mg/L	6030	5085	5430	5515	478
100 mg/L	6420	5655	5925	6000	388

Table B-6. BOD_5 (mg/L) of Leachate A on Day 74

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	Average	Standard Deviation
Control	3540	3760	3630	3643	111
100 µg/L	5860	5000	4605	5155	642
1.0 mg/L	4120	4180	4050	4117	65
100 mg/L	5820	6640	4680	5713	984

Table B-7. BOD_5 (mg/L) of Leachate A on Day 134

[ZnO]	BOD Bottle #1	BOD Bottle #2	Average	Standard Deviation
Control	2496	2634	2565	97.6
100 µg/L	3990	4212	4101	157.0
1.0 mg/L	2982	3066	3024	59.4
100 mg/L	3048	3312	3180	186.7

Table B-8. BOD_5 (mg/L) of Leachate B on Day 0

	BOD Bottle #1	BOD Bottle #2	Average	Standard Deviation
Leachate	617	919	618	2

Table B-9. BOD_5 (mg/L) of Leachate B on Day 40

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	BOD Bottle #4	Average	Standard Deviation
Control	327	459	562	602	488	123
100 µg/L	447	504	692	682	581	124
1.0 mg/L	N\A	N\A	N\A	N\A	N\A	N\A
100 mg/L	342	342	738	448	468	187

Table B-10. BOD_5 (mg/L) of Leachate B on Day 60

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	BOD Bottle #4	Average	Standard Deviation
Control	23.75	15.75	75.75	84.75	50	35
100 µg/L	89	83	56.25	21.75	63	31
1.0 mg/L	197	173	183.75	186.75	185	10
100 mg/L	33	27	33.75	41.25	34	6

Table B-11. BOD_5 (mg/L) of Leachate B on Day 81

[ZnO]	BOD Bottle #1	BOD Bottle #2	BOD Bottle #3	BOD Bottle #4	Average	Standard Deviation
Control	12.75	17.25	8.5	7.5	11	4
100 µg/L	18.75	15.75	6.5	6.5	12	6
1.0 mg/L	6.75	5.25	11.5	12.5	9	4
100 mg/L	14.25	14.25	4.5	8.5	10	5

Table B-12. BOD_5 (mg/L) of Leachate B on Day 102

[ZnO]	BOD Bottle #1	BOD Bottle #2	Average	Standard Deviation
Control	9.8	9.8	9.8	0.0
100 µg/L	4.6	4.1	4.4	3.7
1.0 mg/L	7.2	8.4	7.8	0.4
100 mg/L	2.8	2.6	2.7	2.2

Five-Day Biochemical Oxygen Demand Statistical Significance Analysis

Table B-13. Leachate A BOD_5 Statistical Significance Test for Day 134

BOD_5 Day 134			
	100 µg/L ZnO	1.0 mg/L ZnO	100 mg/L ZnO
BOD_5 Value (mg/L)	4100	3020	3180
$\bar{X}$	4100	3020	3180
µ (control)	2570	2570	2570
S	157	59.4	137
$\sqrt{n}$	1.41	1.41	1.41
df	1	1	1
t	13.78	-10.72	6.31

Table B-14. Leachate B BOD_5 Statistical Significance Test for Day 102

BOD_5 Day 102			
	100 µg/L ZnO	1.0 mg/L ZnO	100 mg/L ZnO
Value (mg/L)	4.38	7.8	2.75
$\bar{X}$	4.38	7.80	2.75
µ (control)	9.83	4.38	7.80
S	3.68	0.35	2.19
$\sqrt{n}$	1.41	1.41	1.41
df	1	1	1
t	-2.10	-8.08	-4.55

Table B-15. Leachate A BOD_5 First-Order Rate Constant Statistical Significance Test

	First-Order Rate Constant (day^{-1})		
	100 µg/L ZnO	1.0 mg/L ZnO	100 mg/L ZnO
$\bar{X}$	0.0072	0.01	0.0085
µ (control)	0.012	0.012	0.012
S	0.00117	0.00166	0.000595
$\sqrt{n}$	1.41	1.41	1.41
df	1	1	1
t	-5.80	-1.70	-8.33

Regression Analysis using MINTAB

Regression Analysis: 100 µg/L ZnO versus Time (days)

The regression equation is
C3 = 9.19 - 0.00716 C1

Predictor Coef SE Coef T P
Constant 9.19060 0.07561 121.56 0.000
Slope -0.007160 0.001170 -6.12 0.002

S = 0.127183 R-Sq = 88.2% R-Sq(adj) = 85.9%

Analysis of Variance

Source DF SS MS F P
Regression 1 0.60534 0.60534 37.42 0.002
Residual Error 5 0.08088 0.01618
Total 6 0.68622

Regression Analysis: 1.0 mg/L ZnO versus Time (days)

The regression equation is
C4 = 9.30 - 0.0104 C1

Predictor Coef SE Coef T P
Constant 9.2959 0.1075 86.51 0.000
Slope -0.010385 0.001664 -6.24 0.002

S = 0.180766 R-Sq = 88.6% R-Sq(adj) = 86.4%

Analysis of Variance

Source DF SS MS F P
Regression 1 1.2733 1.2733 38.97 0.002
Residual Error 5 0.1634 0.0327
Total 6 1.4367

Regression Analysis: 100 mg/L ZnO versus Time (days)

The regression equation is
C5 = 9.23 - 0.00853 C1

Predictor	Coef	SE Coef	T	P
Constant	9.23401	0.03840	240.45	0.000
Slope	-0.0085310	0.0005945	-14.35	0.000

S = 0.0646021 R-Sq = 97.6% R-Sq(adj) = 97.2%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	0.85929	0.85929	205.89	0.000
Residual Error	5	0.02087	0.00417		
Total	6	0.88015			

Table B-16. Leachate B BOD_5 First-Order Rate Constant Statistical Significance Test

	First-Order Rate Constant (day^{-1})		
	100 µg/L ZnO	1.0 mg/L ZnO	100 mg/L ZnO
$\bar{X}$	0.053	0.046	0.057
µ (control)	0.047	0.047	0.047
S	0.012	0.015	0.011
$\sqrt{n}$	1.41	1.41	1.41
df	1	1	1
t	0.720	-0.096	1.25

Regression Analysis: 100 µg/L ZnO versus Time (days)

The regression equation is
C3 = 7.20 - 0.0534 C1

Predictor Coef SE Coef T P
Constant 7.1994 0.7841 9.18 0.003
C1 -0.05338 0.01178 -4.53 0.020

S = 0.923329 R-Sq = 87.3% R-Sq(adj) = 83.0%

Analysis of Variance

Source DF SS MS F P
Regression 1 17.517 17.517 20.55 0.020
Residual Error 3 2.558 0.853
Total 4 20.074

Regression Analysis: 1.0 mg/L ZnO versus Time (days)

The regression equation is
C4 = 7.29 - 0.0498 C1

Predictor Coef SE Coef T P
Constant 7.2851 0.9812 7.42 0.005
C1 -0.04981 0.01474 -3.38 0.043

S = 1.15541 R-Sq = 79.2% R-Sq(adj) = 72.3%

Analysis of Variance

Source DF SS MS F P
Regression 1 15.250 15.250 11.42 0.043
Residual Error 3 4.005 1.335
Total 4 19.255

Regression Analysis: 100 mg/L ZnO versus Time (days)

The regression equation is
C5 = 7.13 - 0.0572 C1

Predictor	Coef	SE Coef	T	P
Constant	7.1250	0.7507	9.49	0.002
C1	-0.05719	0.01128	-5.07	0.015

S = 0.884008 R-Sq = 89.6% R-Sq(adj) = 86.1%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	20.106	20.106	25.73	0.015
Residual Error	3	2.344	0.781		
Total	4	22.451			

Biochemical Methane Potential Summary

Table B-17. Gas Volume (mL) of Leachate A

[ZnO]	Day 28	Day 43	Day 54	Day 77
Control	13.4	4.6	4.5	12.5
100 µg/L	15.2	3.6	9.5	14
1.0 mg/L	9.9	0.6	5.5	15
100 mg/L	16.9	3.6	5.5	9.5

Table B-18. Cumulative Gas Volume (mL) of Leachate A

[ZnO]	Day 28	Day 43	Day 54	Day 77
Control	13.4	18.0	22.5	35.0
100 µg/L	15.2	18.8	28.3	42.3
1.0 mg/L	9.9	10.5	16.0	31.0
100 mg/L	16.9	20.5	26.0	35.5

Table B-19. Gas Quality (Percent Methane) of Leachate A

[ZnO]	Day 28	Day 43	Day 54	Day 77
Control	71	58	56	59
100 µg/L	73	63	60	66
1.0 mg/L	71	35	56	69
100 mg/L	73	66	59	62

Table B-20. Gas Quality (Percent Carbon Dioxide) of Leachate A

[ZnO]	Day 28	Day 43	Day 54	Day 77
Control	29	42	44	41
100 µg/L	27	38	40	34
1.0 mg/L	29	65	44	31
100 mg/L	27	34	41	38

Table B-21. Gas Quality (Percent Methane) of Leachate B

[ZnO]	Day 9	Day 30	Day 50
Control	62	54	61
100 µg/L	39	39	44
1.0 mg/L	40	40	31
100 mg/L	34	47	49

Table B-22. Gas Quality (Percent Carbon Dioxide) of Leachate B

[ZnO]	Day 9	Day 30	Day 50
Control	62	54	61
100 µg/L	61	61	56
1.0 mg/L	60	60	69
100 mg/L	66	53	51

Table B-23. Gas Volume (mL) of Leachate B

[ZnO]	Day 9	Day 30	Day 50
Control	7.5	3.4	0.0
100 µg/L	9.0	4.4	1.3
1.0 mg/L	12.3	5.4	1.8
100 mg/L	10.8	5.9	0.0

Table B-24. Cumulative Gas Volume (mL) of Leachate B

[ZnO]	Day 9	Day 30	Day 50
Control	16.3	19.7	19.7
100 µg/L	17.8	22.2	23.5
1.0 mg/L	21.0	26.5	28.2
100 mg/L	19.5	25.5	25.5

APPENDIX C: SOLIDS DATA

Table C-1. Solid Concentration (mg/L) by Size Fraction Control (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
X>1.5 µm	860	1320	1420	1150	1780
.45<X<1.5 µm	870	183	240	146	1285
0.20<X<.45 µm	21	4667	4560	790	1685
X<0.20 µm	13429	9356	9520	16220	12640
Total	15180	15526	15740	18306	17390

Table C-2. Solid Concentration (mg/L) by Size Fraction 100 µg/L ZnO (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
X>1.5 µm	860	1078	1190	1090	1110
.45<X<1.5 µm	870	5603	5720	397	1549
0.20<X<.45 µm	21	2808	2650	1470	2940
X<0.20 µm	13429	6387	6570	14270	13100
Total	15180	15876	16130	17227	18699

Table C-3. Solid Concentration (mg/L) by Size Fraction 1.0 mg/L ZnO (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
X>1.5 µm	860	1788	1850	1820	2200
.45<X<1.5 µm	870	1824	1760	1970	365
0.20<X<.45 µm	21	3649	3590	1340	502
X<0.20 µm	13429	8396	8620	11080	13200
Total	15180	15657	15820	16210	16267

Table C-4. Solid Concentration (mg/L) by Size Fraction 100 mg/L ZnO (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
X>1.5 µm	860	1687	1710	1270	1640
.45<X<1.5 µm	870	2254	2120	2180	2040
0.20<X<.45 µm	21	3895	3910	770	800
X<0.20 µm	13429	8609	8800	12150	11180
Total	15180	16445	16540	16370	15660

Table C-5. Cumulative Solids Concentration (mg/L) by Size Fraction Control (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
<1,500 nm	14320	14206	14320	18580	15610
<450 nm	13450	14023	14080	17010	11460
<200 nm	13429	9356	9520	16220	12640

Table C-6. Cumulative Solids Concentration (mg/L) by Size Fraction 100 µg/L ZnO (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
<1,500 nm	14320	14798	14940	15740	16040
<450 nm	13450	9195	9220	15740	16040
<200 nm	13429	6387	6570	14270	13100

Table C-7. Cumulative Solids Concentration (mg/L) by Size Fraction 1.0 mg/L ZnO (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
<1,500 nm	14320	13869	13970	14390	14066.67
<450 nm	13450	12045	12210	12420	13702.13
<200 nm	13429	8396	8620	11080	13200

Table C-8 Table C- 9. Cumulative Solids Concentration (mg/L) by Size Fraction 100 mg/L ZnO (Leachate A)

Size Fraction	Day 0	Day 7	Day 21	Day 30	Day 60
<1,500 nm	14320	14758	14830	15100	14020
<450 nm	13450	12504	12710	12920	11980
<200 nm	13429	8609	8800	12150	11180

Table C-10. Solid Concentration (mg/L) by Size Fraction Control (Leachate B)

Size Fraction	Day 0	Day 7	Day 30	Day 60
X>1.5 µm	67	230	555	225
0.45<X<1.5 µm	1574	204	0	0
0.20<X<0.45 µm	46	520	930	104
0.001<X<0.20 µm	865	536	0	219
X<0.001 µm	2800	2284	3600	3167
Total	5352	3774	5085	3715

Table C-11. Solid Concentration (mg/L) by Size Fraction 100 µg/L ZnO (Leachate B)

Size Fraction	Day 0	Day 7	Day 30	Day 60
X>1.5 µm	67	180	845	265
0.45<X<1.5 µm	1574	0	260	3491
0.20<X<0.45 µm	46	1240	365	52
0.001<X<0.20 µm	865	504	520	281
X<0.001 µm	2800	1786	2050	2896
Total	5352	3710	4040	6985

Table C-12. Solid Concentration (mg/L) by Size Fraction 1.0 mg/L ZnO (Leachate B)

Size Fraction	Day 0	Day 7	Day 30	Day 60
X>1.5 µm	67	333	1180	1090
0.45<X<1.5 µm	1574	0	340	0
0.20<X<0.45 µm	46	132	240	104
0.001<X<0.20 µm	865	1308	870	73
X<0.001 µm	2800	1875	1310	3292
Total	5352	3649	3940	4559

Table C-13. Solid Concentration (mg/L) by Size Fraction 100 mg/L ZnO (Leachate B)

Size Fraction	Day 0	Day 7	Day 30	Day 60
X>1.5 µm	67	780	1200	940
0.45<X<1.5 µm	1574	340	90	209
0.20<X<0.45 µm	46	1390	170	151
0.001<X<0.20 µm	865	670	1360	160
X<0.001 µm	2800	1130	1250	3000
Total	5352	4310	4070	4460

Table C-14. Cumulative Solids Concentration (mg/L) by Size Fraction Control (Leachate B)

Size Fraction	Day 0	Day 7	Day 30	Day 60
<1,500 nm	5285	3544	4530	3490
<450 nm	3711	3340	4530	3490
<1.0 nm	2800	2284	3600	3167

Table C-15. Cumulative Solids Concentration (mg/L) by Size Fraction 100 µg/L ZnO (Leachate B)

Size Fraction	Day 0	Day 7	Day 30	Day 60
<1,500 nm	5285	3530	3195	6720
<450 nm	3711	3530	2935	3229
<1.0 nm	2800	1786	2050	2896

Table C-16. Cumulative Solids Concentration (mg/L) by Size Fraction 1.0 mg/L ZnO (Leachate B)

Size Fraction	Day 0	Day 7	Day 30	Day 60
<1,500 nm	5285	3316	2760	3469
<450 nm	3711	3316	2420	3469
<1.0 nm	2800	1875	1310	3292

Table C-17. Cumulative Solids Concentration (mg/L) by Size Fraction 100 mg/L ZnO

Size Fraction	Day 0	Day 7	Day 30	Day 60
<1,500 nm	5285	3530	2870	3520
<450 nm	3711	3190	2780	3311
<1.0 nm	2800	1130	1250	3000

APPENDIX D: METALS ANALYSIS

Table D-1. Zn^{2+} Concentration by Size Fractions of Leachate B

Sample	Day 0 Concentration (mg/L)	Day 7 Concentration (mg/L)	Day 30 Concentration (mg/L)
1.0 nm	0.34	0.73	1.11
200 nm	0.04	0.01	1.22
450 nm	0	0.49	0.89
1500 nm	0.13	1.67	3.46

Table D-2. Zn^{2+} Concentration by Size Fractions of Leachate C

Sample	Day 0 Concentration (mg/L)	Day 7 Concentration (mg/L)	Day 30 Concentration (mg/L)
1.0 nm	0.25	0.029	0.068
200 nm	0	0.12	0.093
450 nm	0.02	0.034	0.047
1500 nm	0.02	2.26	1.014

Table D-3. Zn^{2+} Concentration by Size Fractions of Leachate D

Sample	Day 0 Concentration (mg/L)	Day 7 Concentration (mg/L)	Day 30 Concentration (mg/L)
1.0 nm	0.39	0.48	0.33
200 nm	0.11	0.5	0.17
450 nm	0.16	0.52	0.22
1500 nm	0	1.98	3.05

Table D-4. Cumulative Zn^{2+} Concentration by Size Fractions of Leachate B

	Day 0 Concentration (mg/L)	Day 7 Concentration (mg/L)	Day 30 Concentration (mg/L)
<1.0 nm	0.34	0.73	1.11
<450 nm	0.38	1.23	3.22
<1,500 nm	0.51	2.9	6.68

Table D-5. Cumulative Zn^{2+} Concentration by Size Fractions of Leachate C

	Day 0 Concentration (mg/L)	Day 7 Concentration (mg/L)	Day 30 Concentration (mg/L)
<1.0 nm	0.25	0.029	0.068
<450 nm	0.27	0.183	0.208
<1,500 nm	0.29	2.44	1.22

Table D-6. Cumulative Zn^{2+} Concentration by Size Fractions of Leachate D

	Day 0 Concentration (mg/L)	Day 7 Concentration (mg/L)	Day 30 Concentration (mg/L)
<1.0 nm	0.39	0.48	0.33
<450 nm	0.66	1.5	0.72
<1,500 nm	0.66	3.48	3.77

Table D-7. Total Mass Balance of Zn (mg)

	Mass of Zn (mg)		
	470 mL Fraction	30 mL Fraction	Total
Beaker #1	37.7	1.04	38.8
Beaker #2	38.0	2.10	40.1
Beaker #3	38.5	0.64	39.1
Beaker #4	37.8	1.74	39.5
Beaker #5	38.4	2.12	40.6
Average	38.1	1.53	39.6

Table D-8. Percent Recovery (%) of Zn

	Percent Recovery (30 mL)*	Percent Recovery (470 mL)*	Percent Recovery (Total)
Beaker #1	3%	94%	97%
Beaker #2	5%	95%	100%
Beaker #3	2%	96%	98%
Beaker #4	4%	94%	99%
Beaker #5	4%	96%	100%
Average	4%	95%	99%

* Percent calculated based on mass of Zn added (50 mg ZnO equals ~40 mg Zn)

APPENDIX E: VISUAL MINTEQA CHEMICAL ZINC SPECIES RESULTS

Table E-1. Concentrations and Activities of Aqueous Species Leachate B on Day 0

	Concentration (M)	Activity	Log activity
Zn DOM1	5.07E-06	4.48E-06	-5.348
$Zn(CO_3)_2^{-2}$	2.28E-09	1.05E-09	-8.979
$Zn(NH_3)_2^{+2}$	3.92E-10	1.81E-10	-9.743
$Zn(NH_3)_3^{+2}$	5.15E-11	2.38E-11	-10.624
$Zn(NH_3)_4^{+2}$	3.12E-12	1.44E-12	-11.842
$Zn(OH)_2$ (aq)	2.49E-10	2.52E-10	-9.599
$Zn(OH)_3^-$	3.22E-14	2.66E-14	-13.576
$Zn(OH)_4^{-2}$	3.04E-19	1.40E-19	-18.853
$Zn(SO_4)_2^{-2}$	3.03E-12	1.40E-12	-11.855
Zn^{+2}	3.90E-08	1.80E-08	-7.745
Zn_2OH^{+3}	5.65E-17	9.90E-18	-17.004
$ZnCl^+$	5.81E-10	4.79E-10	-9.32
$ZnCl_2$ (aq)	4.13E-12	4.18E-12	-11.379
$ZnCl_3^-$	5.26E-14	4.33E-14	-13.363
$ZnCl_4^{-2}$	4.34E-16	2.00E-16	-15.699
$ZnCO_3$ (aq)	5.54E-08	5.60E-08	-7.252
$ZnHCO_3^+$	2.41E-08	1.98E-08	-7.703
$ZnHPO_4$ (aq)	3.45E-10	3.49E-10	-9.458
$ZnNH_3^{+2}$	3.60E-09	1.66E-09	-8.78
$ZnOH^+$	6.75E-10	5.56E-10	-9.255
$ZnSO_4$ (aq)	7.79E-10	7.88E-10	-9.104

Table E-2. Concentrations and Activities of Aqueous Species Leachate B on Day 7

	Concentration (M)	Activity	Log activity
Zn DOM1	1.09E-05	9.61E-06	-5.017
$Zn(CO_3)_2^{-2}$	5.24E-09	2.41E-09	-8.617
$Zn(NH_3)_2^{+2}$	9.00E-10	4.15E-10	-9.382
$Zn(NH_3)_3^{+2}$	1.18E-10	5.46E-11	-10.263
$Zn(NH_3)_4^{+2}$	7.17E-12	3.31E-12	-11.481
$Zn(OH)_2$ (aq)	5.73E-10	5.79E-10	-9.237
$Zn(OH)_3^-$	7.41E-14	6.10E-14	-13.214
$Zn(OH)_4^{-2}$	7.00E-19	3.23E-19	-18.491
$Zn(SO_4)_2^{-2}$	6.96E-12	3.21E-12	-11.494
Zn^{+2}	8.97E-08	4.14E-08	-7.383
Zn_2OH^{+3}	2.99E-16	5.23E-17	-16.281
$ZnCl^+$	1.34E-09	1.10E-09	-8.958
$ZnCl_2$ (aq)	9.50E-12	9.60E-12	-11.018
$ZnCl_3^-$	1.21E-13	9.96E-14	-13.002
$ZnCl_4^{-2}$	9.98E-16	4.60E-16	-15.337
$ZnCO_3$ (aq)	1.27E-07	1.29E-07	-6.89
$ZnHCO_3^+$	5.53E-08	4.56E-08	-7.341
$ZnHPO_4$ (aq)	7.93E-10	8.01E-10	-9.096
$ZnNH_3^{+2}$	8.27E-09	3.82E-09	-8.418
$ZnOH^+$	1.55E-09	1.28E-09	-8.893
$ZnSO_4$ (aq)	1.79E-09	1.81E-09	-8.742

Table E-3. Concentrations and Activities of Aqueous Species Leachate B on Day 30

	Concentration (M)	Activity	Log activity
Zn DOM1	1.65E-05	1.46E-05	-4.836
$Zn(CO_3)_2^{-2}$	8.50E-09	3.92E-09	-8.407
$Zn(NH_3)_2^{+2}$	1.46E-09	6.74E-10	-9.171
$Zn(NH_3)_3^{+2}$	1.92E-10	8.87E-11	-10.052
$Zn(NH_3)_4^{+2}$	1.16E-11	5.37E-12	-11.27
$Zn(OH)_2$ (aq)	9.30E-10	9.40E-10	-9.027
Zn(OH)3-	1.20E-13	9.91E-14	-13.004
$Zn(OH)_4^{-2}$	1.14E-18	5.24E-19	-18.281
$Zn(SO_4)_2^{-2}$	1.13E-11	5.21E-12	-11.283
Zn^{+2}	1.46E-07	6.71E-08	-7.173
Zn_2OH^{+3}	7.87E-16	1.38E-16	-15.861
$ZnCl^{+}$	2.17E-09	1.79E-09	-8.748
$ZnCl_2$ (aq)	1.54E-11	1.56E-11	-10.807
$ZnCl_3^{-}$	1.96E-13	1.62E-13	-12.791
$ZnCl_4^{-2}$	1.62E-15	7.47E-16	-15.127
$ZnCO_3$ (aq)	2.07E-07	2.09E-07	-6.68
$ZnHCO_3^{+}$	8.98E-08	7.40E-08	-7.131
$ZnHPO_4$ (aq)	1.29E-09	1.30E-09	-8.886
$ZnNH_3^{+2}$	1.34E-08	6.19E-09	-8.208
$ZnOH^{+}$	2.52E-09	2.08E-09	-8.683
$ZnSO_4$ (aq)	2.91E-09	2.94E-09	-8.532

Table E-4. Concentrations and Activities of Aqueous Species Leachate C on Day 0

	Concentration (M)	Activity	Log activity
Zn DOM1	3.81E-06	3.21E-06	-5.493
$Zn(CO_3)_2^{-2}$	2.27E-09	7.87E-10	-9.104
$Zn(NH_3)_2^{+2}$	3.84E-10	1.33E-10	-9.877
$Zn(NH_3)_3^{+2}$	2.12E-10	7.33E-11	-10.135
$Zn(NH_3)_4^{+2}$	5.37E-11	1.86E-11	-10.731
$Zn(OH)_2$ (aq)	2.34E-11	2.41E-11	-10.618
$Zn(OH)_3^-$	5.02E-15	3.85E-15	-14.415
$Zn(OH)_4^{-2}$	8.89E-20	3.08E-20	-19.512
$Zn(SO_4)_2^{-2}$	6.63E-14	2.30E-14	-13.639
Zn^{+2}	2.17E-09	7.52E-10	-9.124
Zn_2OH^{+3}	2.85E-19	2.62E-20	-19.582
$ZnCl^+$	2.43E-11	1.86E-11	-10.73
$ZnCl_2$ (aq)	1.47E-13	1.51E-13	-12.82
$ZnCl_3^-$	1.90E-15	1.46E-15	-14.836
$ZnCl_4^{-2}$	1.81E-17	6.28E-18	-17.202
$ZnCO_3$ (aq)	9.62E-09	9.91E-09	-8.004
$ZnHCO_3^+$	3.02E-09	2.32E-09	-8.635
$ZnHPO_4$ (aq)	1.18E-11	1.21E-11	-10.916
$ZnNH_3^{+2}$	8.41E-10	2.91E-10	-9.536
$ZnOH^+$	4.59E-11	3.52E-11	-10.454
$ZnSO_4$ (aq)	2.00E-11	2.06E-11	-10.685

Table E-5. Concentrations and Activities of Aqueous Species Leachate C on Day 7

	Concentration (M)	Activity	Log activity
Zn DOM1	4.41E-07	3.73E-07	-6.429
$Zn(CO_3)_2^{-2}$	2.63E-10	9.10E-11	-10.041
$Zn(NH_3)_2^{+2}$	4.44E-11	1.54E-11	-10.814
$Zn(NH_3)_3^{+2}$	2.45E-11	8.47E-12	-11.072
$Zn(NH_3)_4^{+2}$	6.22E-12	2.15E-12	-11.667
$Zn(OH)_2$ (aq)	2.71E-12	2.79E-12	-11.555
$Zn(OH)_3^-$	5.80E-16	4.45E-16	-15.352
$Zn(OH)_4^{-2}$	1.03E-20	3.56E-21	-20.449
$Zn(SO_4)_2^{-2}$	7.67E-15	2.65E-15	-14.576
Zn^{+2}	2.51E-10	8.70E-11	-10.061
Zn_2OH^{+3}	3.81E-21	3.50E-22	-21.456
$ZnCl^+$	2.81E-12	2.16E-12	-11.667
$ZnCl_2$ (aq)	1.70E-14	1.75E-14	-13.757
$ZnCl_3^-$	2.20E-16	1.69E-16	-15.773
$ZnCl_4^{-2}$	2.10E-18	7.26E-19	-18.139
$ZnCO_3$ (aq)	1.11E-09	1.15E-09	-8.941
$ZnHCO_3^+$	3.49E-10	2.68E-10	-9.572
$ZnHPO_4$ (aq)	1.36E-12	1.40E-12	-11.853
$ZnNH_3^{+2}$	9.72E-11	3.37E-11	-10.473
$ZnOH^+$	5.31E-12	4.07E-12	-11.39
$ZnSO_4$ (aq)	2.32E-12	2.39E-12	-11.622

Table E-6. Concentrations and Activities of Aqueous Species Leachate C on Day 30

	Concentration (M)	Activity	Log activity
Zn DOM1	1.04E-06	8.74E-07	-6.059
$Zn(CO_3)_2^{-2}$	6.17E-10	2.13E-10	-9.671
$Zn(NH_3)_2^{+2}$	1.04E-10	3.60E-11	-10.443
$Zn(NH_3)_3^{+2}$	5.74E-11	1.99E-11	-10.702
$Zn(NH_3)_4^{+2}$	1.46E-11	5.05E-12	-11.297
$Zn(OH)_2$ (aq)	6.35E-12	6.54E-12	-11.184
$Zn(OH)_3^-$	1.36E-15	1.04E-15	-14.981
$Zn(OH)_4^{-2}$	2.41E-20	8.35E-21	-20.078
$Zn(SO_4)_2^{-2}$	1.80E-14	6.23E-15	-14.206
Zn^{+2}	5.90E-10	2.04E-10	-9.69
Zn_2OH^{+3}	2.10E-20	1.93E-21	-20.715
$ZnCl^+$	6.59E-12	5.06E-12	-11.296
$ZnCl_2$ (aq)	3.98E-14	4.10E-14	-13.387
$ZnCl_3^-$	5.16E-16	3.96E-16	-15.402
$ZnCl_4^{-2}$	4.92E-18	1.70E-18	-17.768
$ZnCO_3$ (aq)	2.61E-09	2.69E-09	-8.57
$ZnHCO_3^+$	8.20E-10	6.29E-10	-9.201
$ZnHPO_4$ (aq)	3.20E-12	3.29E-12	-11.482
$ZnNH_3^{+2}$	2.28E-10	7.90E-11	-10.103
$ZnOH^+$	1.24E-11	9.55E-12	-11.02
$ZnSO_4$ (aq)	5.44E-12	5.60E-12	-11.252

Table E-7. Concentrations and Activities of Aqueous Species Leachate D on Day 0

	Concentration (M)	Activity	Log activity
Zn DOM1	5.94E-06	5.03E-06	-5.299
$Zn(CO_3)_2^{-2}$	1.52E-09	5.32E-10	-9.274
$Zn(NH_3)_2^{+2}$	1.64E-10	5.76E-11	-10.24
$Zn(NH_3)_3^{+2}$	4.29E-11	1.51E-11	-10.822
$Zn(NH_3)_4^{+2}$	5.16E-12	1.81E-12	-11.742
$Zn(OH)_2$ (aq)	1.43E-11	1.47E-11	-10.832
$Zn(OH)_3^-$	1.72E-15	1.32E-15	-14.879
$Zn(OH)_4^{-2}$	1.69E-20	5.94E-21	-20.226
$Zn(SO_4)_2^{-2}$	1.42E-13	4.99E-14	-13.302
Zn^{+2}	4.13E-09	1.45E-09	-8.838
Zn_2OH^{+3}	5.78E-19	5.48E-20	-19.261
$ZnCl^+$	4.69E-11	3.61E-11	-10.443
$ZnCl_2$ (aq)	2.86E-13	2.94E-13	-12.532
$ZnCl_3^-$	3.70E-15	2.85E-15	-14.546
$ZnCl_4^{-2}$	3.50E-17	1.23E-17	-16.91
$ZnCO_3$ (aq)	1.10E-08	1.13E-08	-7.946
$ZnHCO_3^+$	6.12E-09	4.71E-09	-8.327
$ZnHPO_4$ (aq)	2.10E-11	2.16E-11	-10.665
$ZnNH_3^{+2}$	7.58E-10	2.66E-10	-9.575
$ZnOH^+$	4.96E-11	3.82E-11	-10.418
$ZnSO_4$ (aq)	4.11E-11	4.23E-11	-10.374

Table E-8. Concentrations and Activities of Aqueous Species Leachate D on Day 7

	Concentration (M)	Activity	Log activity
Zn DOM1	7.31E-06	6.19E-06	-5.209
$Zn(CO_3)_2^{-2}$	1.87E-09	6.55E-10	-9.184
$Zn(NH_3)_2^{+2}$	2.02E-10	7.09E-11	-10.149
$Zn(NH_3)_3^{+2}$	5.28E-11	1.85E-11	-10.732
$Zn(NH_3)_4^{+2}$	6.36E-12	2.23E-12	-11.651
$Zn(OH)_2$ (aq)	1.76E-11	1.81E-11	-10.742
$Zn(OH)_3^-$	2.11E-15	1.63E-15	-14.789
$Zn(OH)_4^{-2}$	2.08E-20	7.32E-21	-20.136
$Zn(SO_4)_2^{-2}$	1.75E-13	6.14E-14	-13.212
Zn^{+2}	5.09E-09	1.79E-09	-8.748
Zn_2OH^{+3}	8.77E-19	8.32E-20	-19.08
$ZnCl^+$	5.78E-11	4.45E-11	-10.352
$ZnCl_2$ (aq)	3.52E-13	3.62E-13	-12.441
$ZnCl_3^-$	4.56E-15	3.51E-15	-14.455
$ZnCl_4^{-2}$	4.31E-17	1.51E-17	-16.82
$ZnCO_3$ (aq)	1.36E-08	1.39E-08	-7.856
$ZnHCO_3^+$	7.53E-09	5.80E-09	-8.237
$ZnHPO_4$ (aq)	2.59E-11	2.66E-11	-10.575
$ZnNH_3^{+2}$	9.34E-10	3.28E-10	-9.484
$ZnOH^+$	6.11E-11	4.70E-11	-10.328
$ZnSO_4$ (aq)	5.06E-11	5.21E-11	-10.283

Table E-9. Concentrations and Activities of Aqueous Species Leachate D on Day 30

	Concentration (M)	Activity	Log activity
Zn DOM1	5.03E-06	4.25E-06	-5.371
$Zn(CO_3)_2^{-2}$	1.28E-09	4.50E-10	-9.347
$Zn(NH_3)_2^{+2}$	1.39E-10	4.87E-11	-10.313
$Zn(NH_3)_3^{+2}$	3.63E-11	1.27E-11	-10.895
$Zn(NH_3)_4^{+2}$	4.36E-12	1.53E-12	-11.815
$Zn(OH)_2$ (aq)	1.21E-11	1.24E-11	-10.905
$Zn(OH)_3^-$	1.45E-15	1.12E-15	-14.952
$Zn(OH)_4^{-2}$	1.43E-20	5.02E-21	-20.299
$Zn(SO_4)_2^{-2}$	1.20E-13	4.22E-14	-13.375
Zn^{+2}	3.50E-09	1.23E-09	-8.911
Zn_2OH^{+3}	4.13E-19	3.92E-20	-19.407
$ZnCl^+$	3.96E-11	3.05E-11	-10.515
$ZnCl_2$ (aq)	2.42E-13	2.49E-13	-12.605
$ZnCl_3^-$	3.13E-15	2.41E-15	-14.618
$ZnCl_4^{-2}$	2.96E-17	1.04E-17	-16.983
$ZnCO_3$ (aq)	9.30E-09	9.57E-09	-8.019
$ZnHCO_3^+$	5.17E-09	3.98E-09	-8.4
$ZnHPO_4$ (aq)	1.78E-11	1.83E-11	-10.738
$ZnNH_3^{+2}$	6.41E-10	2.25E-10	-9.648
$ZnOH^+$	4.20E-11	3.23E-11	-10.491
$ZnSO_4$ (aq)	3.48E-11	3.58E-11	-10.447

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